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Europäisches Patent Nr.: 0143537
European patent No.:
Brevet européen n°:

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Europäisches Patentamt
European Patent Office
Office européen des brevets

Publication number:

0 143 537
B1

12

EUROPEAN PATENT SPECIFICATION

45 Date of publication of patent specification: 21.03.90

51 Int. Cl.⁵: **B 01 D 53/04**

71 Application number: **84306709.1**

72 Date of filing: **02.10.84**

54 **Method and apparatus for gas separation and synthesis.**

20 Priority: **03.10.83 US 538370**

43 Date of publication of application:
05.06.85 Bulletin 85/23

45 Publication of the grant of the patent:
21.03.90 Bulletin 90/12

64 Designated Contracting States:
DE FR GB IT NL SE

55 References cited:
US-A-3 262 277
US-A-3 871 179
US-A-4 354 859

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Courier Press, Leamington Spa, England.

EP 0 143 537 B1

Description

Background of the invention

Field of the invention

The invention relates generally to separations and catalytic chemical reactions conducted in the gas or vapour phase. Some particular applications include gas separation or purification combined with waste heat recovery, generation of already compressed and preheated oxygen for combustion, natural gas purification and compression, hydrogen isotope separation, ammonia or methanol synthesis, and steam reforming of methane.

Prior art

Gas separation by pressure swing adsorption is achieved by cyclic flow of a gas mixture over an adsorbent bed which more readily adsorbs a fraction of the mixture. The term "swings" refers to periodic variations of pressure. The total pressure, i.e. sum of partial pressures of the gases, is elevated during intervals of flow in a first direction and is reduced during alternating intervals of flow in the reverse direction. According to the well known parametric pumping separation principle, the less readily adsorbed fraction tends to migrate in the first direction over complete cycles while the more readily adsorbed fraction tends to migrate in the reverse direction.

The conventional process for gas separation by pressure swing adsorption uses two or more adsorbent beds with directional valving to control the flow of compressed feed gas over each bed in alternating sequence, while the other bed is purged at low pressure by the reverse flow of a portion of the product gas. This conventional process makes inefficient use of mechanical energy, because the compression energy of the feed gas is largely dissipated over the valves. Another common name for pressure swing adsorption gas separation is "heatless adsorption", which seems to deny the possibility of a beneficial effect by thermal coupling to heat sources or heat sinks to improve pressure swing adsorption apparatus as disclosed in the present invention.

Conventional gas separation processes (including pressure swing adsorption, cryogenic distillation and membrane permeation) are powered by mechanical energy. The energy intensiveness of air separation is a major obstacle to widen use of enriched oxygen in high temperature processes such as solid fuel gasification. An efficient air separation process powered by waste heat would address this need.

Some secondary and adverse thermal effects do arise in operation of conventional pressure swing adsorption gas separation apparatus, particularly those using large adsorption beds with poor heat exchange to ambient. The adverse effects include cyclic release and take-up of the latent heat of adsorption which causes a temperature swing of the adsorbent bed which acts in opposition to the pressure swing. Adsorption is

increased by higher pressure and/or reduced temperature, and conversely is decreased by lower pressure and/or higher temperatures.

Examples of single bed pressure swing adsorption devices are found in U.S. Pat. No. 3,121,625 (Broughton), U.S. Pat. No. 3,164,454 (Wilson), U.S. Pat. No. 3,236,028 (Rutan), U.S. Pat. No. 4,169,715 (Eriksson), U.S. Pat. No. 4,194,892 (Jones et al), U.S. Pat. No. 4,207,084 (Gardner), and U.S. Pat. No. 4,354,859 (Keller et al). Most of the above references use mechanical volume displacement means at one or both ends of the adsorbent bed to generate cyclic flow and pressure variations in the bed. The Keller patent uses mechanical volume displacement means at both ends of the adsorbent bed, with a specified range of phase angles between the two volume displacement means of unequal displacement. None of these references contemplates the integral coupling of a pressure swing adsorption process with a regenerative thermal power or heat pump cycle as in the present invention.

A temperature swing adsorption separation process known as "recuperative parametric pumping" was described by Wilhelm (R. H. Wilhelm, A. W. Rice and A. R. Bendelius, Ind. Eng. Chem. Fundamentals 5, 441, (1966) with applications to liquid phase separation. A fluid mixture was made to flow cyclically in forward and reverse directions in an adsorbent bed with an imposed thermal gradient between hot and cold ends. The heat capacity of the fluid mixture was large with respect to the heat capacity of the adsorbent material, in order to obtain thermal cycling of each adsorbent pellet.

The present invention can be considered as subjecting a flow of a gas mixture to a Stirling cycle or other thermodynamic regenerative cycle which has been changed to operate as an *open cycle* to perform thermally coupled pressure swing adsorption separations. This contrasts with a conventional Stirling cycle machine which has a *closed* working volume filled with a gaseous working fluid. The working volume includes hot and cold spaces, whose volume is varied by mechanical volume displacement means reciprocating out of phase. A thermal regenerator is in the flow path connecting the hot and cold spaces. In a conventional Stirling machine heat capacity of the working fluid is desirably very low with respect to the heat capacity of the regenerator materials so that the temperature swing at each point of the regenerator will be minimal. This temperature swing of the regenerator results in non-isothermal conditions in the regenerator and is an unavoidable source of inefficiency in conventional Stirling type machine.

The out of phase reciprocation of the volume displacement means causes cyclic flow of the working fluid through the regenerator. Cyclic pressure variations are associated with alternative heating or cooling of gas flowing respectively into the hot or cold spaces, and with variations of total working volume. If volume changes in the hot space have a leading phase with respect to

volume changes in the cold space, the Stirling machine is an engine. Conversely, the Stirling machine is a heat pump or refrigerator when volume changes in the hot space lag volume changes in the cold space. Related machines include thermocompressors, Vuilleumier thermally powered refrigeration machines, and Gifford-McMahon pressure powered refrigeration machines.

In Stirling type machines operated as cryogenic refrigerators, performance deteriorates at very low temperatures where the heat capacity of regenerator materials ceases to be very large relative to the heat capacity of the helium gas working fluid. As disclosed in U.S. Patent 3,262,277 (Nesbitt), a solid adsorbent material can improve performance of thermal regenerators operating below 20 degrees K, as the effective heat capacity is increased by the presence of adsorbed helium in the regenerator material. Under the steady state operating conditions envisaged by Nesbitt, the adsorbed helium phase is essentially static, contrary to the requirements of a gas separation or purification process. Significant rates of cyclic adsorption and desorption would entail corresponding release and take-up of a latent heat of adsorption, degrading regenerator thermal performance in a Stirling type refrigerator. Successful operation of the Nesbitt patent depends on suppression of cyclic pressure swing adsorption and desorption through substantial cancellation by opposing temperature swing effects over the adsorbent in the regenerator, and probably also through capillary condensation of liquid helium in adsorbent pores which causes known pressure hysteresis effects inhibiting desorption from pores filled with liquid adsorbate. High speed operation may also tend to suppress cyclic adsorption and desorption.

Use of rapidly dissociating gases such as nitrogen tetroxide as working fluid in Brayton and Stirling closed cycle engines is proposed in U.S. Patent No. 3,370,420 (Johnson). The dissociation/recombination reaction increases gas volume in the hot space and thus improves engine work ratio. Use of a catalyst in the regenerator of a Stirling engine using a dissociated gas working fluid has been proposed in U.S. Pat. No. 3,871,179 (Bland) with the object of obtaining enhanced reaction rates in closed cycle Stirling engines with high work ratio. In these inventions, the forward reaction is exactly cancelled by the reverse reaction over each cycle because reaction products are trapped in the engine spaces. As there is no means to drive the reaction off equilibrium, these inventions cannot be applied to chemical synthesis processes. Therefore it has not hitherto been possible to apply the closed Stirling cycle to recover heat from exothermic chemical synthesis reactions, or to supply heat for endothermic reactions, while using the reacting gases as the Stirling machine working fluid.

Fundamental problems in chemical process industry include the removal of reaction product

species and exothermic reaction heat from catalyst beds. High temperatures promote good reaction rates, but shift the equilibrium of an exothermic reaction toward lower conversion. These problems and their conventional solutions are exemplified by the important chemical process of ammonia synthesis, which proceeds by the exothermic reaction:—



This reaction takes place over a promoted iron catalyst at a typical pressure of 200 atmospheres and a typical temperature of 750 degrees K. The hydrogen and nitrogen feed gases are stringently purified (apart from minor amounts of "inert" gases such as argon and methane, which are non-reactive in the ammonia synthesis loop, and are compressed to the high working pressure. In order to remove the product and thus drive the synthesis reaction over the catalyst bed off equilibrium, the gas mixture of reagents and produced ammonia is recirculated between the hot catalyst bed and a cool ammonia separator/condenser. This recirculation requires a recycle compressor and a recuperative heat exchanger. To prevent excessive catalyst heating from the exothermic reaction, temperature control is achieved either by energy inefficient quenching by injection of cool feed gas, or by heat exchange to an external waste heat recovery power cycle. A Brayton cycle gas turbine heat recovery approach for ammonia synthesis is disclosed in U.S. Pat. No. 4,224,299 (Barbet et al) and U.S. Pat. No. 4,273,743 (Barber et al). Unless the synthesis loop operates at very high pressure, a refrigeration plant is needed to condense liquid ammonia at the cool end of the synthesis loop. Means are provided for purging accumulated inerts from the loop, and valuable hydrogen from the purge gas.

Considerable research attention has been devoted to improving productivity or selectivity of catalytic chemical reactors through cyclic operation forced by periodic variation of feed composition or temperature cycling. For example, it was found by (A. K. Jain, Ph.D. Thesis, University of Waterloo Ontario) that forced feed composition cycling at periods of several minutes improved the productivity of the ammonia synthesis reaction. However operation of the ethylene hydrogenation reaction over a nickel catalyst with pulsating pressure and flow was tested by Baiker et al (A. Baiker and W. Richarz, Chem. Ing. Tech 48, 1203, (1976)), who found that catalyst productivity was reduced relative to steady state operation. While it has been shown that in many cases cyclic operation can improve reaction productivity or selectivity under laboratory conditions, there remains a need for full scale reactors capable of beneficially exploiting a wide range of periodic phenomena which may be based on cyclic composition, temperature, flow or pressure variations.

Chromatographic effects have been found to enable some catalytic reactions to be driven

According to a second aspect of the invention, there is provided a process of operating a modified Stirling cycle machine wherein an internal working volume containing a gas has a flow path containing first and second spaces and a thermal regenerator disposed between the spaces, the first and second spaces being at different temperatures to expose the regenerator to a thermal gradient, the process including the steps of:

cyclically reversing direction of flow of the gas along the flow path so that direction of flow alternates between opposite ends of the flow path; and

cyclically varying pressure of the gas between upper and lower pressure limits within the working volume so that a phase relationship exists between the cyclic pressure variations and cyclic flow reversals relative to the thermal regenerator, the process being characterized by:

(a) providing between the spaces an adsorbent bed containing adsorbent material to cooperate with the thermal regenerator to produce an adsorbent/regenerator combination;

(b) introducing into the working volume a gas mixture containing a first component which is more readily adsorbed by the adsorbent material, and a second component which is less readily adsorbed by the adsorbent material;

(c) generating the cyclic pressure variations and the cyclic flow reversals by first cyclic gas volume displacements associated with the first space and by second cyclic gas volume displacements associated with the second space such that the first cyclic gas volume displacements have a leading phase angle with respect to the second cyclic gas volume displacements;

(d) simultaneously when coordinating the phase relationship between the cyclic pressure variations and the cyclic flow reversals relative to the regenerator combination, preferentially adsorbing and immobilising the first component on the combination bed by increased pressure when the gas flows in one direction, and preferentially desorbing the first component by decreasing the pressure when the flow direction is reversed; and

(e) removing from one end of the regenerator combination a first gas fraction enriched in the first component, and removing from the opposite end of the regenerator combination a second gas fraction depleted in the first component, thereby also achieving conversion between thermal energy and compression energy in the gas mixture.

According to a third aspect of the invention, there is provided an apparatus for separating components of a gas mixture containing a first component which is more readily adsorbed and a second component which is less readily adsorbed by an adsorbent material, the apparatus including a body having an internal working volume having first and second spaces, a flow path inter-connecting the first and second spaces, and an adsorbent bed containing the adsorbent material and provided in the flow path between the spaces, inlet means to admit gas mixture into the working

volume, and outlet means to discharge gas from adjacent opposite ends of the adsorbent bed, volume displacement means associated with the first and second spaces, reciprocating means cooperating with the volume displacement means so as to produce cyclic variations in total pressure and cyclic reversals in direction of flow of the gas, the reciprocating means determining a phase relationship between the cyclic variations of pressure in the gas and the directions of flow of the gas over the adsorbent bed, so that flow under reduced pressure past the adsorbent bed towards one space is enriched in the first more readily adsorbed component, while reverse flow under increased pressure past the adsorbent bed towards the opposite space is depleted in the first more readily adsorbed component, the apparatus being further characterised by:

(a) a thermal regenerator cooperating with the adsorbent bed to produce an adsorbent/regenerator combination provided in the flow path between the spaces to receive flow which passes along the flow path,

(b) means for maintaining the first and second spaces at different temperatures to expose the regenerator combination to a thermal gradient, so as to subject the gas flow to cyclical reversals of temperature together with the cyclical reversals of pressure and direction of flow so as to facilitate separation of the gas mixture into a first gas fraction enriched in the first component, and a second gas fraction enriched in the second component,

(c) the reciprocating means cooperating with the first and second volume displacement means so that the displacement means reciprocate at the same frequency, and the volume of gas displaced by the first volume displacement means leads the volume of gas displaced by the second volume displacement means by a phase angle of between zero degrees and 180 degrees.

According to a fourth aspect of the invention, there is provided an apparatus which resembles a modified Stirling cycle machine, the apparatus including a body having an internal working volume having first and second spaces, a flow path for gas inter-connecting the first and second spaces, a thermal regenerator provided in the flow path between the first and second spaces, the first and second spaces being at different temperatures to expose the regenerator to a thermal gradient, first and second volume displacement means communicating with the first and second spaces respectively, reciprocating means cooperating with the first and second volume displacement means so that the first and second volume displacement means reciprocate at the same frequency to produce cyclic variations in total pressure and in direction of flow of the gas, the reciprocating means determining phase angle between cyclic variations of pressure in the gas and flow directions of the gas over the regenerator, the apparatus being characterized by:

(a) an adsorbent bed containing adsorbent

displacer thermocompressor pressure swing adsorption apparatus,

Figure 6 is a simplified schematic of a thermally coupled pressure swing adsorption apparatus with two displacers,

Figure 7 is a simplified schematic of a gas separation apparatus powered by a heat source, with a portion of the adsorbent/regenerator combination being cooled,

Figure 8 is a simplified schematic of an improved gas synthesis apparatus based on the invention.

Detailed disclosure

Figure 1

A Stirling cycle machine 10 has a single acting power piston 11 reciprocating in a power cylinder 12, and a double-acting displacer piston 13 reciprocating in a displacer cylinder 14. The power cylinder encloses a variable volume 15 sealed by a high pressure piston seal 16.

The displacer piston 13 is driven by a displacer rod 17 having a cross sectional area which is small with respect to the cross sectional area of displacer cylinder 14. The displacer rod 17 is sealed by a high pressure gland seal 18. The displacer piston 13 divides the internal volume of displacer cylinder 14 between a variable volume 19 adjacent the gland seal 18 and a variable volume 20. The variable volume 19 is connected to the variable volume 15 by a conduit means 21. The variable volume 20 is the expansion volume or the first space of the Stirling machine, while the sum of the variable volumes 15 and 19 is the compression volume or the second space of the machine. The pistons 11 and 13 serve as a first volume displacement means and a second volume displacement means, respectively, which communicate with the first space 20, and with the second space (15 and 19) respectively.

The variable volume 20 is connected by a conduit means 24 to a first heat exchanger 25 maintained at a temperature T_1 , which in turn is connected to a thermal regenerator 27 by conduit means 28. The variable volume 19 is connected by conduit means 30 to a second heat exchanger 32 maintained at a temperature T_2 which will often approximate ambient temperature, which in turn is connected to the thermal regenerator 27 by a conduit means 33. It is evident that gas within the expansion volume or first space, i.e. volume 20 and the conduits 24 and 28 will be maintained approximately at temperature T_1 , while gas within the compression volume or second space, i.e. volumes 15 and 19, and the conduits 30 and 33 will be maintained approximately at temperature T_2 . It can be seen that a temperature or thermal gradient between T_1 and T_2 will be maintained across the regenerator 27 between the connections to conduits 28 and 33. The volumes 15, 19 and 20, the conduits and associated heat exchangers and the thermal regenerator provide a flow path of the apparatus, which has a working volume. While the heat exchangers 25 and 32 are shown spaced from the cylinders enclosing the

respective volumes, following conventional Stirling cycle machine design, the heat exchangers could be incorporated into the cylinder walls.

A reciprocating means 35 interconnects rods 36 and 19 of the pistons 11 and 13 so that the pistons are reciprocated at the same frequency and with suitable phase such as that an increase (or decrease) of the expansion volume leads an increase (or decrease) of the compression volume. Hence upwards motion of the displacer piston 13 leads upwards motion of the power piston 11. The Stirling machine will then operate to convey heat from the heat exchanger 25 to heat exchanger 32 i.e., there is a net transport of heat from the expansion space to the compression space. If T_1 is greater than T_2 , first and second ends 41 and 42 of the regenerator are associated with relatively hot and relatively cold spaces respectively, and the machine will function as an engine, delivering work from the power piston 11. Conversely, if T_2 is greater than T_1 , the ends 41 and 42 are associated with relatively cold and hot spaces respectively and the machine will operate as a heat pump or refrigerator, absorbing work from the power piston 11.

In a conventional Stirling engine, the regenerator contains finely divided material with high heat capacity and large surface area, arranged to adsorb and store heat from gas flowing through the regenerator with efficient heat transfer and low flow friction. In order to achieve the purposes of the invention, the regenerator 27 also contains fixed adsorbent material 34 which preferentially adsorbs a first component of a feed gas mixture relative to a less readily adsorbed second component, in the operating pressure and temperature regime, both of which vary cyclically within the reversing flows of gas as will be described.

Hence the regenerator includes an adsorbent bed of a sorbent which provides a sorption function, such as surface adsorption, bulk adsorption and desorption. The adsorbent material may be mixed with non-adsorbent material, and different adsorbent materials or mixtures of material may be used in zones of the regenerator operating at different temperature levels. Alternatively, all of the material in the regenerator may be the adsorbent material which then also provides the full heat storage function. For particular applications as will be described with reference to Figure 8, some of the adsorbent may also have catalytic properties with respect to reactions of mixing gas components. Particularly in heat pump or refrigerator embodiment, the heat capacity of the solid material must be large with respect to the heat capacity of the working fluid. The regenerator and the adsorbent bed cooperate to produce an adsorbent/regenerator combination but the term "regenerator", "adsorbent bed", and "bed" and "regenerator combination" are used interchangeably in this specification except where so stated.

The adsorbent or catalyst bed may be a packed bed of pellets, fibres or granular material, which

(a) the ratio of maximum pressure to minimum pressure inside the machine;

(b) the phase relationship between gas flow velocities and pressure at each point in the regenerator;

(c) the ratio of each cyclic distance travelled by gas particles in the regenerator to length of the regenerator.

It will be noted that the reciprocating means 35 or piston drive mechanism of the Figure 1 Stirling machine has not been described in detail. Numerous Stirling machine crank mechanisms and also free piston configurations are known in the prior art, and may be used in conjunction with this invention. Likewise, numerous alternative arrangements of compression and expansion volume displacement means are known such as diaphragms or liquid pistons. The power and displacer pistons may occupy a single cylinder. Separate compression and expansion cylinders may provide the equivalent function of power and displacer cylinders. Compression and expansion cylinders may be compounded in multi-cylinder double-acting Stirling machines. Also, the regenerator may be installed inside the displacer piston of displacer type machines. For purposes of this invention, the above and other prior art Stirling machines configurations are equivalent.

While the Stirling cycle manifestly incorporates cyclic changes in both pressure and gas velocity, it is not immediately evident that a favourable regime for pressure swing adsorptive separation is in fact available. A general theoretical foundation for the present invention is found in a theorem (based on an ideal Stirling machine with isothermal expansion and compression, perfect heat exchange and no friction) correlating flow direction of any point of the regenerator with the pressure extremes. At the cycle pressure maximum, the direction of flow will be from the compression volume toward the expansion volume at all points in the regenerator. At the cycle pressure minimum, the flow direction is from the expansion volume to the compression volume. This theorem is valid for the ideal Stirling cycle machine for all possible parameters of temperature ratio, volume displacement ratio, displacement phase angle and dead volume ratio. Consequently net heat i.e. heat transported over a complete cycle, and the preferentially adsorbed gas component will be transported toward the compression volume or second space in the present invention, while the less readily adsorbed gas component will be transported toward the expansion volume or first space, the relationship of the volumes or spaces being determined by the phase relationship as described.

Operation

As stated previously, the Stirling cycle machine 10 can operate either as an engine producing net work from the power piston 11, and/or a portion of compression work from the gases discharged from the regenerator. Alternatively it can function as a heat pump or refrigerator, absorbing work

from the piston 11. When operating in either mode as above, the reciprocating means 35 coordinates the phase relationship between the cyclic pressure variations and the cyclic flow reversals relative to the adsorbent bed so that the volume of gas displaced by the displacer piston 13, the first volume displacement means, leads the volume of gas displaced by the power piston 11, the second volume displacement means. Hence, the volume displacement means coordinates the phase relationship between the pressure and flow reversals such that cyclic gas volume displacements adjacent the first space or the first end 41 of the bed have a leading displacement phase angle with respect to cyclic gas volume displacements adjacent the second space or opposite second end 42 of the bed. This produces the cyclic variations in total pressure and cyclic reversals in direction of flow over the bed so that flow of a first gas fraction under reduced pressure past the bed towards one end of the bed or flow path is enriched in the first more readily adsorbed component, while reverse flow of a second gas fraction under increased pressure past the bed towards the opposite end of the flow path is depleted in the first more readily adsorbed component. This is because the first component is preferentially adsorbed and immobilised by increased pressure on the adsorbent bed when the gas flows in one direction, and the first component is preferentially desorbed when the pressure is decreased and the flow is reversed. The first gas fraction enriched in the more readily adsorbed first component is removed from one end of the bed, while the second gas fraction enriched in the less readily adsorbed component is removed from the opposite end of the bed.

Whether the apparatus is operating either as an engine, a heat pump or refrigerator, the phasing of pressure and the flow cycle is such that, when pressure is at the upper limit for a particular cycle of pressure, the direction of the bulk flow of gas is towards the expansion volume, that is towards the variable volume 20. Similarly, when pressure is at a lowermost point of its cycle, the corresponding direction of bulk flow of the gas is towards the compression volume, that is towards the variable volumes 15 and 19. Also, the Stirling engine or pump can be considered as a means of transporting heat in a particular direction through a complete cycle. This is referred to as a net transport of heat, and in the present invention, it has been found that the net transport of heat moves in the direction of flow of the preferentially adsorbed component, that is towards the compression volume, the variable volumes 15 and 19.

In summary, the invention has the dual function of transporting heat and the preferentially adsorbed component in one direction, while transporting the less readily adsorbed gas component in the reverse direction across a temperature or thermal gradient. If the heat is transported in the direction of the lower temperature, the apparatus functions as an engine. If the heat is transported in the direction of the higher

outline as 86. In the present invention, this temperature swing tends to increase the desorption induced by the pressure minimum, but will itself be cancelled in part by cooling induced by the latent heat of desorption. Conversely, at the moment of maximum pressure, the flow per arrow 84 is towards the compression space 20 and the adsorption induced by the pressure swing tends to be reinforced by a downward temperature swing of the bed shown as broken line 87, which is not cancelled by the latent heat of adsorption. In prior art Stirling engines, the temperature swing effect would be as shown by the broken lines 86 and 87 in Figure 3, which would contribute to efficiency losses, without the aforesaid compensating effect of the invention associated with the latent heat of adsorption. Hence the engine embodiment of the present invention offers improvements both to the effectiveness of the adsorption process, and also to the cycle thermodynamic efficiency in this aspect. An arrow 88 represents direction of net heat transport.

Figure 4 is an analogous temperature profile for a heat pump embodiment in which the expansion space 20 is at T_1 which is lower than the compression space 15, 19 which is at T_2 . In a conventional Stirling cycle heat pump, there is an upward temperature swing 91 and a corresponding downward temperature swing 92, both shown in broken outline. The upper temperature swing now arises with the maximum pressure flow, shown in direction of arrow 94, which is in opposition to the desired adsorption. The amplitude of the temperature swing will be increased further by the release of latent heat by pressure swing induced adsorption. Hence, in the heat pump embodiment the temperature swing is adverse to gas separation effectiveness and to cycle thermodynamic efficiency. It will thus be desirable to provide high heat capacity in the heat pump regenerator so as to minimise the actual temperature swing. The arrow 88 again represents direction of net heat transport.

Adsorbent selectivity between the gas components has an effect on the operation of this invention. The term "preferentially" as used herein refers to a component that is more readily adsorbed relative to a second component when the adsorbed molar concentration of the first species changes relatively more strongly with varying partial pressure of the first species, while the adsorbed molar concentration of the second species changes relatively less strongly with varying partial pressure of the second species. The above occurs within the operating regime of pressures, temperatures, gas compositions and cycle speeds over a particular portion of the adsorbent bed. This definition relates selectivity to the active adsorption and desorption of gas species under pressure swings, as opposed to the static capacity of the adsorbent bed under some average condition.

In the case of high adsorbent selectivity between gas components and/or large capacity of the adsorbent bed, the velocity of the concentration wave front will be a small fraction of the gas

velocity. Then a relatively short adsorbent bed can achieve good separation, without "break through" of the wave front beyond the regenerator. Break through would cause mixing to reduce the separation achieved. The finite width of the concentration wave front must be considered in design optimization.

In the case of low adsorbent selectivity between gas components and/or large capacity of the adsorbent bed, the velocity of the concentration wave front will more closely approach that of the gas velocity. Break through of the wave front can be avoided or minimized by using a relatively low phase angle between compression and expansion displacements, and/or by using a relatively high dead volume (within the regenerator) which will reduce attainable pressure ratio. It may be desired to reduce the adsorbent capacity (for example by admixture with non-adsorbent material, or by use of thin adsorbent coatings) in order that the machine more closely approach the operating characteristics of a conventional Stirling machine, with gas separation as a secondary role.

Some examples of specific applications of the Figure 1 embodiment are now described.

Example No. 1

Oxygen separation from air may be achieved using a zeolite such as molecular sieve 13X, which adsorbs nitrogen more readily than oxygen. Air is introduced through the inlet valve 39. An oxygen enriched gas fraction will be produced through the outlet valve 46, while a nitrogen enriched fraction will be produced through the outlet valve 43. If temperature T_2 is ambient temperature and heat is supplied to the heat exchanger 25 such that temperature T_1 is greater than temperature T_2 , the machine is a Stirling engine which will deliver mechanical work after losses are taken into account. With the adsorbent operating at elevated temperatures, it will be necessary to use a relatively high mean working pressure to achieve adequate adsorbent loading and selectivity. Thus air entering inlet valve 39 must be already compressed.

Conversely if the heat exchanger 25 is at a lower than ambient temperature i.e., temperature T_1 is less than temperature T_2 the machine can be a combined refrigeration and dehydration and air separation plant. The refrigerator will actively reduce temperature T_1 below ambient until the cooling load including thermal leakage is in balance with the machine's cooling capacity. The heat rejection temperature T_2 and the position of the feed injection point 54 in regenerator 27 are designed to ensure that the temperature at the feed injection point is above zero degrees centigrade, to prevent frost formation in the regenerator. Then water, carbon dioxide and nitrogen will be concentrated toward the outlet valve 43 at the warmer portion of the apparatus, while oxygen will be concentrated to the outlet valve 46 at the colder end.

In this case it will be appropriate to operate at a much lower mean working pressure than in the

described first and second volume displacement means are combined into the first double-acting displacer piston or means 106 so that the phase angle between the first and second displacer means is 180 degrees. This results in the compression volume and expansion volume being almost equal and 180 degrees out of phase. The machine can be either operated as an engine, in which case T_1 is higher than T_2 , or as a heat pump or refrigerator, in which case T_2 is greater than T_1 . As there is no power piston, only modest pressure ratios can be achieved even with high temperature ratios unless one of the components changes phase while in the regenerator combination 119, 120. In operation of the engine, there will be a substantial phase difference between pressure variations and flow in the regenerator, approaching 90 degrees in the limit of zero feed throughput when the apparatus ceases to deliver any useful work. This phase difference is reduced in a preferred operation mode in which the outlet valve 139 is opened by the control means 40 during the lowest pressure interval of the cycle. Phase shift between pressure and regenerator flow can be further reduced by increasing feed throughput, at a penalty of reduced pressure ratio. In effect, this process involves converting a portion of the heat supplied to the relatively hot space to compression work by delivering at least a portion of the separated gas fraction at elevated pressure relative to the pressure at which the feed gas mixture is introduced into the process.

Example No. 4

This Fig. 5 embodiment has the advantage of extreme simplicity. Its use will be attractive in applications where a highly adsorbed contaminant is to be removed from a gas which is also to be compressed. For example, well head natural gas compression can be combined with purification to remove hydrogen sulphide, water and carbon dioxide, while the gas itself is compressed through a modest pressure ratio. In this particular example, the heat source to power the apparatus may be provided by combustion of the waste gas stream.

In view of the substantial phase shift in the regenerator between pressure and flow, this embodiment may be applied more favourably to separations where adsorptive selectivity is controlled by rate effects, since regenerator flow will be approximately in phase with the time rate of change of pressure.

A simple modification to the Fig. 5 embodiment 102 is to substitute the non-return valves 123 and 128 for positively timed, two-wave valves which are also controlled by the control means 140, by undesignated connections shown in broken outline. This alternative apparatus may be operated in close analogy to a Gifford-McMahon cooling machine. In this alternative, temperature T_2 may be ambient, and temperature T_1 is greater than T_2 . The apparatus is now powered by compression energy of a pressurised feed gas mixture introduced through the inlet valve 128 in the inlet

conduit 126. The valve 128 is opened after the displacer piston 106 is extended to an outer portion of the stroke so that the compression space 113 is at its maximum and the pressure is fairly low and the outlet valve 139 is closed. The entering feed gas mixture through the conduit 126 compresses gas already in the compression space 113 until the valve 123 is opened by the control means to deliver some product gas fraction depleted in the more readily adsorbed component. The pressure in the conduit 125 is now slightly less than the supply pressure in the conduit 126. The inlet valve 128 is closed, and the displacer piston 106 is retracted to the bottom of its stroke, displacing gas from the compression space 113 to flow through the regenerator 119 into the space 111 with cooling over the regenerator and through a consequent pressure drop. The outlet valve 139 is then opened, reducing pressure further and delivering gas enriched in the more adsorbed component. When the pressure in the system is reduced to the minimum level, the valve 139 is closed and the displacer 111 retracts to displace gas from the space 113 through the regenerator to the space 111, becoming warmer and thus providing an initial pressure rise to complete the cycle.

The Gifford-McMahon cycle has a major advantage that high pressure ratios can be imposed externally, but, unlike other embodiments, has the disadvantage of relatively low thermal efficiency because of irreversible gas expansion.

Fig. 6

A third embodiment of the invention 148 utilises two similar displacer and regenerator combinations, within a single working volume, in which the two displacers are operated out of phase. The apparatus has a flow path having generally similar first and second portions 150 and 151 respectively which resemble a flow path portion of the Fig. 5 embodiment and have first and second displacer cylinders 153 and 154 with first and second double-acting displacers 155 and 156 respectively. The displacers 155 and 156 have respective rods 159 and 160 which cooperate with a reciprocating means 162 to reciprocate the displacers within the respective cylinders at equal frequencies but phased apart. The first displacer 155 divides the cylinder 153 into a first space or an expansion space 163 and a second or compression space 165. The displacer 156 divides the cylinder 154 into a first space or expansion space 168 and a second space or compression space 170. A connecting conduit 172 interconnects the compression spaces 165 and 170 so that pressure throughout the embodiment 148 is essentially equalised.

A first thermal regenerator 175 has a first end 176 connected by conduits 176 and 177 to the expansion and compression spaces respectively of the first cylinder 153. Heat exchangers 178 and 179 at temperatures T_1 and T_2 cooperate with the conduits 176 and 177 respectively to maintain the adjacent spaces at the particular temperatures of

displacer 156 leads the displacer 155 by about 90 degrees of phase. The refrigeration effect will be delivered partly as cooling load at the heat exchanger 178, and partly as a cold compressed gas delivered from the non-return outlet valve 184.

It is evident by comparison with the previous embodiment that alternative design selections of inlet and outlet valves, associated heat recovery coils and the feed injection location, not shown specifically, in the regenerator combination 175 are admissible within the scope of this invention and that features of the particular embodiments shown may be interchanged.

In summary, the refrigeration alternative of the Fig. 6 embodiment differs from the thermo-compressor embodiment mainly in the thermal gradients imposed on the regenerator. The regenerator combination 175 of the first portion, which has the adsorbent 189, has a thermal gradient defined by first and second temperatures in which the first temperature is lower than the second temperature and the second temperature is near ambient. However the second portion of the flow path has the second thermal regenerator 190 (without an adsorbent) and is subjected to a second thermal gradient defined by the second temperature T_2 and the third temperature T_3 , in which the third temperature is elevated above ambient. Various means to supply heat to the apparatus at the third temperature are provided, so as to drive the displacer and reciprocating means in such a manner as to obtain gas separation together with refrigeration functions.

Fig. 7

A fourth embodiment 201 of the invention is for gas separation, and may be coupled together in series or in parallel to provide multiple separation steps of a complex process. Furthermore, as will be described with reference to Fig. 8, this invention, as well as the previously described embodiments, can also be used for chemical reactions. The fourth embodiment shows direct coupling of an engine with a refrigerator within a single Stirling cycle machine. One particular use of this embodiment is to deliver hot compressed oxygen to a high temperature combustion process, in which the machine can be powered entirely by waste heat from the combustion process, thus avoiding the high cost of mechanical energy required for conventional air separation processes.

The embodiment 201 includes a stepped displacer cylinder 203 having outer and inner cylinder portions 205 and 206, in which the portion 205 is smaller in diameter than the portion 206. A stepped displacer 208 is complementary to the inner and outer cylinder portions and has a displacer rod 209 which is sealed at 210. A power piston 212 is reciprocable within a power cylinder 214 and a conduit 216 interconnects of variable volume 215 of the power cylinder with the inner cylinder portion 206. The piston 212 has a piston rod 219 which, similarly to the rod 209 cooperates

with a reciprocating means 221 which reciprocates the piston 212 and the displacer 208 within their respective cylinders, at a similar frequency but phased apart. The displacer 208 divides the internal volume of the displacer cylinder 203 into a variable volume 225 in the outer cylinder portion, a variable volume 227 adjacent the lower portion of the inner cylinder portion 206, and a third variable volume 229 in a portion of the displacer cylinder which bridges the inner and outer portions. Similarly to the Stirling engine embodiment described with reference to Fig. 1, the variable volume 225 is the expansion volume or first space, and the sum of the variable volumes 215 and 227 is the compression volume of the machine and is termed the second space. The third variable volume or space 229 communicates with an intermediate conduit 231 connected adjacent an intermediate portion 232 of the displacer cylinder bridging the inner and outer portions thereof.

The embodiment 201 has a flow path including a conduit 233 extending from the first space 225, through a heat exchanger 235 to a first end of a thermal regenerator 238 containing an adsorbent bed 239, which cooperate to produce an adsorbent/regenerator combination as before. The flow path also includes a conduit 240 having a heat exchanger 241 in which the conduit 240 communicates an opposite end of the regenerator combination 238 with the variable volume 227 or second space.

An inlet conduit 243 having an inlet valve 245 supplies feed gas to the interior of the thermal regenerator/adsorbent bed. Outlet conduits 248 and 247 provided with outlet valves 250 and 251 respectively communicate with opposite second and first ends 252 and 249 respectively of the regenerator combination.

With the exception of the stepped displacer 208, it can be seen that the structure above described closely resembles the Stirling cycle machine as described with reference to Fig. 1. The embodiment 201 differs mainly by the provision of the third space 229 and the intermediate conduit 231 which communicates with an intermediate combination portion 253 of the regenerator combination 238, 239. The regenerator combination has the intermediate portion 255 disposed between the opposite ends of the regenerator, so that first and second combination portions 255 and 256 extend between the intermediate portion and the first and second ends of the regenerator. In operation, the reciprocating means 221 reciprocates the displacer 208 and power piston 212 to function as volume displacement means so that the displacer 208 leads the piston 212 as before described. This provides cyclical reversal of flow and variations of pressure on the bed. The displacement means communicates also with the third space 229 to produce cyclical reversals in direction of flow of the gas between the third space and the intermediate portion. Due to relative diameters of the portions of the displacer 208, the mass flow in the second portion 256 is greater

product separation in liquid form. A lower portion of the power cylinder 271 acts as a liquid separator 302 and has a liquid discharge valve 304 which is opened periodically to remove liquid product of the reaction. A purge valve 306 positioned above the separator 302 is open periodically to discharge "inert" gases which might otherwise accumulate in the power piston. In applications where the product of the reaction does not liquefy, or purging of inert gases is not a problem, the previously described power cylinder and power piston of Fig. 1 could be substituted for that shown in Fig. 8.

A major feature of the embodiment 266 is the provision of means to permit reaction of two or more gases within the reaction zone of the working volume, and removal of one or more components of the reaction to increase conversion rate. Because the rate of many gas phase chemical reactions is enhanced by use of a catalyst, in most cases it is preferable to provide a catalyst in the reaction zone where the chemical reaction is to take place. For example, if the gas phase reaction is an exothermic reaction, which liberates heat, the catalyst is best provided in the higher temperature portion of the apparatus, for example in the expansion or first space 274 where it is shown as a matrix 308. If the gas phase reaction is endothermic, which absorbs heat, the catalyst would best be provided in a second space 275 of the apparatus, and receives heat transported from the first space. Clearly, separate spaces for the reaction can be provided if necessary, the catalyst adjacent either end of the regenerator, or anywhere in the flow path at an appropriate temperature. The reaction zone is usually associated with a variable volume space which can remove exothermic heat or provide endothermic heat of reaction.

Example No. 6

A particularly useful application of the embodiment 266, using an exothermic reaction, is the synthesis of ammonia from nitrogen and hydrogen over a promoted iron catalyst. In this reaction, the regenerator combination 282, 283 contains an adsorbent which preferentially adsorbs ammonia relative to hydrogen and nitrogen, for example a zeolite such as molecular sieve 13X. The feed gases of nitrogen and hydrogen in correct proportions are fed into the inlet conduit 290, purified by the purifier 291 with the exception of minor "inert" gases such as argon and methane, and compressed in the compressor 293 to an operating pressure of about 120 atmospheres. The compressed feed gas is delivered through the inlet valve 295 to the heat exchanger 296 which heats the feed gas to the synthesis temperature T_1 of about 450 degrees C. The preheated feed gas is injected into the conduit 284 of the Stirling engine through the non-return valve 298 and passes through the heat exchanger 286 which serves as a start-up heater.

The catalyst in the expansion volume 274 enhances the speed of the reaction so that the

product, ammonia gas, is transported by pressure swing adsorption towards the second space or cooler end of the apparatus, that is towards the cooler end of the regenerator, through the conduit 285 where it is condensed in the compression space 275 by removing heat with the heat exchanger 287. Liquid ammonia condenses in the separator 302 from where it is removed during intervals of high pressure through the discharge valve 304. It is added that any liquid ammonia remaining in the separator during intervals of lower pressure would tend to evaporate and thus reduce the amplitude of pressure swings in the systems. Conversely, the presence of some freely mobile liquid ammonia (i.e. droplets in the gas mixture, in the cooler end of the regenerator would tend to increase the amplitude of pressure swings.

The zeolite adsorbent in the regenerator 282 has much higher affinity for ammonia than for hydrogen or nitrogen. However, nitrogen and "inert" gases including argon and methane will be preferentially adsorbed relative to hydrogen. Hydrogen is parametrically pumped into the reaction zone adjacent the hotter end 273. Hence a concentration gradient will be established across the regenerator with the nitrogen and "inerts" more concentrated toward the cold end where the ammonia is also concentrated and liquefied. Excessive build up of inerts will be avoided by periodic opening of the purge valve 306, which will vent the nitrogen rich mixture containing accumulated "inerts" from the separator 302.

It is anticipated that cyclic pressure excursions in this Stirling engine apparatus may range from 120 atmospheres to 200 atmospheres. Since average pressure is than 160 atmospheres, while feed gas injection is 120 atmospheres in this case, it can be seen that the engine actually performs the final stage of feed gas compression within its own regime of cyclic pressure.

At this relatively low synthesis loop pressure of 160 atmospheres, a conventional ammonia synthesis plant could not obtain satisfactory condensation of liquid ammonia without auxiliary refrigeration. In this invention, the lower temperature T_2 will correspond to normal ambient temperatures, and refrigeration is not required because ammonia is concentrated within the apparatus. It is expected that the pressure swing adsorption function will remove ammonia very rapidly from the expansion volume of the engine, driving the reaction far from equilibrium and thus enhancing catalyst productivity.

In ammonia synthesis, the desired product, i.e., ammonia, is adsorbed and removed from the reaction zone by adsorption followed by liquefying and removal as a liquid. In other reactions, if an undesirable side product is formed in a side reaction, the side reaction can be suppressed by preventing the side product from leaving the reaction zone, thus maintaining the side reaction at equilibrium. An example of this type of reaction is given in Example No. 7. In both cases, the process of the invention is thus characterized by

ammonia synthesis can be enhanced by cyclic variations of feed composition. In the present invention, a non-uniform admixture of hydrogen and nitrogen is obtained in the regenerator combination through pressure swing adsorption. Because nitrogen is much less highly adsorbed than ammonia, the characteristic velocity of nitrogen concentration wave front will be faster than the velocity of ammonia concentration wave front. Hence, the machine can be designed so that at least partial break through of the nitrogen concentration wave front back into the catalyst is obtained. Then feed composition cycling over the catalyst will be obtained to some degree by the changing concentration of nitrogen. It will be evident that feed composition cycling may be further enhanced in this invention by separately timed and/or located injection of the feed components. Beneficial chromatographic effects may then be obtained, particularly if adsorbent with high capacity for ammonia is mixed with the catalyst as proposed by Unger and Rinker. In conventional ammonia synthesis plants, feed composition cycling appears to be impracticable because most of the gas flowing through the synthesis loop is recycled.

It will be apparent that many variations to the embodiment of Figure 8 are admissible within this invention. For example, the feed gas could be injected directly into the second or cooler end of the regenerator combination 282 without the heat exchanger 296. This might make control of reactant composition over the catalyst more difficult, but would provide the advantage that any trace carbon dioxide, carbon monoxide and water contaminants would be concentrated by parametric pumping into the ammonia and purge gas effluents, providing some protection to the catalyst.

With appropriately selected catalyst, the embodiment of Figure 8 can be applied directly to methanol synthesis and many other chemical reactions. An important case is Fischer-Tropsch synthesis of hydrocarbons from carbon monoxide and hydrogen reactants, for which the Figure 8 embodiment can favourably influence selectivity between alternative products according to their relative ability to be adsorbed on the selected adsorbent material. Both exothermic and endothermic reactions may be conducted inside Stirling cycle machines based on this invention with changes as discussed previously.

This invention clearly has a wide range of chemical reaction applications, and can be expressed in all embodiments above and in, many embodiments or combinations not limited to those described above.

Claims

1. A process for separating components of a gas mixture containing a first component which is more readily adsorbed and a second component which is less readily adsorbed by an adsorbent material, the process including the steps of:

introducing (37, 126, 181, 243, 290) the gas mixture into a working volume having a flow path containing the adsorbent material (34, 120, 189, 239, 283) within an adsorbent bed;

5 cyclically reversing direction of flow of the gas mixture along the flow path so that direction of the flow alternates between opposite ends of the flow path, cyclically varying the total pressure of the gas mixture between upper and lower pressure limits within the working volume;

10 simultaneously coordinating a phase relationship between the cyclic pressure variations and the cyclic flow reversals relative to the adsorbent bed such that the first component is preferentially adsorbed and immobilized by increased pressure on the adsorbent bed when the gas flows in one direction (72), and the first component is preferentially desorbed when the pressure is decreased and the flow is reversed (73);

15 removing from adjacent one end (42, 133, 180, 252, 276) of the adsorbent bed a first gas fraction enriched in the first component, and removing from adjacent the opposite end (41, 118, 174, 255, 273) of the adsorbent bed a second gas fraction depleted in the first component;

20 providing in the flow path first (20, 111, 163, 225, 274) and second (15, 19, 113; 165; 208, 215; 275, 277) spaces disposed adjacent opposite ends of the regenerator combination, the spaces being at different temperatures to expose the regenerator combination to a thermal gradient; and

30 passing the flow of gas through the spaces in series with the regenerator combination; the process being characterised by:

35 providing in the flow path a thermal regenerator (27, 119, 175, 238, 282) to cooperate with the adsorbent bed to produce an adsorbent/regenerator combination (34, 27; 120, 119; 189, 175; 239, 238; 283, 282);

40 passing through the adsorbent/regenerator combination the flow which passes along the flow path; and

45 generating the cyclic pressure variations and the cyclic flow reversals by first cyclic gas volume displacements associated with the first space (20, 111, 163, 225, 274) and by second cyclic gas volume displacements associated with the second space (15, 19; 113; 165; 208, 215; 275, 277), such that the first cyclic gas volume displacements have a leading phase angle with respect to the second cyclic gas volume displacements, so as to subject the gas flow to cyclical reversals of temperature, together with the cyclical reversals of pressure and direction flow, so as to facilitate separation of the gas into the first and second fractions, and achieve conversion between thermal energy and compression energy in the gas mixture.

50 2. A process of operating a modified Stirling cycle machine wherein an internal working volume containing a gas has a flow path containing first (20, 111, 163, 225, 274) and second (15, 19; 113; 165; 208, 215; 275, 277) spaces and a thermal regenerator (27, 119, 175, 238, 282) dis-

the combination the first gas fraction enriched in the more readily adsorbed first component, and removing from adjacent the first end of the combination the second gas fraction depleted in the first component,

(c) conveying heat from the first space to the second space so as to operate as a heat pump cycle or a refrigeration cycle.

9. A process as claimed in claim 8 further characterised by:

(a) insulating (60) the first space (20), the first end (41) of the regenerator combination, and a portion (24, 28) of the flow path extending between the first space and the first end to permit attainment of low temperatures in the first end of the combination to facilitate gas separation.

10. A process as claimed in any preceding claim, further characterised by:

(a) coordinating the phase relationship between the pressure and flow reversals to generate first cyclic gas volume displacements adjacent a first end (118, 174) of the regenerator combination (119, 120; 175, 189) which have a leading displacement phase angle of 180° with respect to second cyclic gas volume displacements generated adjacent the opposite second end (133, 180) of the regenerator combination and maintaining the working volume substantially constant,

(b) converting a portion of the heat supplied to the relatively hot space (111, 163) to compression work by delivering at least one separated gas fraction at an elevated pressure relative to the pressure at which the gas mixture is introduced into the process, so as to operate as a thermo-compressor cycle.

11. A process as claimed in claim 1 further characterised by:

(a) in a first portion (150) of the flow path, coordinating the phase relationship between the pressure and flow reversals to generate first cyclic gas volume displacements adjacent a first end (174) of the regenerator combination which have a leading displacement phase angle of 180° with respect to second cyclic gas volume displacements generated adjacent the opposite second end of the combination, and maintaining the working volume of the first portion substantially constant,

(b) in a second portion (151) of the flow path, providing a second thermal regenerator (190), and generating within the second portion of the flow path a cyclically reversing direction of flow so that the direction of flow alternates between opposite ends of the second flow path, and subjecting the second regenerator to a thermal gradient so as to cyclically vary pressure of the gas between upper and lower pressure limits, so that a second phase relationship exists in the second portion wherein first cyclic gas volume displacements generated adjacent a first end of the second regenerator (190) have a leading displacement phase angle of 180° with respect to second cyclic gas volume displacements genera-

ted adjacent the opposite second end of the second regenerator, and maintaining the second working volume to be substantially constant,

(c) communicating the first and second portions (150, 151) of the flow path to attain a desired phase relationship between the flow direction reversals and pressure variations of the first and second portions of the apparatus, so as to provide greater flexibility and pressure differences for use as a thermo-compressor.

12. A process as claimed in claim 11 further characterised by:

(a) providing in the second portion (151) of the flow path reversals of larger volumes of gas than in the first portion (150) of the flow path, so that pressure variations from the second portion will dominate the first portion.

13. A process as claimed in claim 11 or 12 further characterised by:

(a) providing in the regenerator combination (175, 189) of the first portion (150) and in the thermal regenerator (190) of the second portion (151) essentially equal thermal gradients having essentially equal upper temperatures (T_1 , T_3) and essentially equal lower temperatures (T_2) in which the first space (163, 168) of each portion is exposed to the upper temperature, so as to operate as a thermo-compressor with enhanced phase relationship.

14. A process as claimed in claim 11 or 12 further characterised by:

(a) in the first portion (150) of the flow path, providing a thermal gradient for the regenerator combination (175, 189) between upper (T_1) and lower temperatures (T_2), wherein the first space (163) is exposed to the lower temperature,

(b) in the second portion (151) of the apparatus, providing in the second regenerator (190) a second thermal gradient in which the first space (168) is exposed to a third temperature (T_3) which is higher than the upper temperature (T_1) of the first portion, so as to operate as a Vuilleumier refrigerator or heat pump, so as to obtain gas separations at low temperatures.

15. A process as claimed in claim 1 or 2 further characterised by:

(a) providing communication with the regenerator combination (238, 239) at an intermediate combination portion (253) between opposite first and second ends (249, 252) of the regenerator combination so that first and second combination portions 255, 256) extend between the intermediate portion (253) and first and second ends of the regenerator combination respectively,

(b) cyclically reversing direction of flow at the intermediate combination portion so as to cyclically vary flow through the first and second combination portions.

16. A process as claimed in claim 15 further characterised by:

(a) maintaining the cyclical reversals of flow at the intermediate combination portion (253) in phase with the cyclical reversals of flow relative to the first end (249) of the regenerator combina-

reversals of temperature together with the cyclical reversals of pressure and direction of flow so as to facilitate separation of the gas mixture into a first gas fraction enriched in the first component, and a second gas fraction enriched in the second component,

(c) the reciprocating means (35, 110, 162, 221, 281) cooperating with the first and second volume displacement means so that the displacement means reciprocate at the same frequency, and the volume of gas displaced by the first volume displacement means leads the volume of gas displaced by the second volume displacement means by a phase angle of between zero degrees and 180 degrees.

26. An apparatus (10, 102, 148, 201, 266) which resembles a modified Stirling cycle machine, the apparatus including a body having an internal working volume having first (20, 111, 163, 225, 274) and second (15, 19; 113; 165; 215, 227; 275, 277) spaces, a flow path for gas inter-connecting the first and second spaces, a thermal regenerator (27, 119, 175, 238, 282) provided in the flow path between the first and second spaces, the first and second spaces being at different temperatures (T_1 , T_2) to expose the regenerator to a thermal gradient, first (13, 106, 155, 208, 269) and second (11, 106, 156, 212, 272) volume displacement means communicating with the first and second spaces respectively, reciprocating means (35, 110, 162, 221, 281) cooperating with the first and second volume displacement means so that the first and second volume displacement means reciprocate at the same frequency to produce cyclic variations in total pressure and in direction of flow of the gas, the reciprocating means determining phase angle between cyclic variations of pressure in the gas and flow directions of the gas over the regenerator, the apparatus being characterised by:

(a) an adsorbent bed containing adsorbent material (34, 120, 189, 239, 283) cooperating with the thermal regenerator to produce an adsorbent/regenerator combination (27, 34; 119, 120; 175, 189; 238, 239; 282, 283) disposed between the first and second spaces,

(b) the gas being a gas mixture containing a first component which is more readily adsorbed and a second component which is less readily adsorbed by the adsorbent material,

(c) inlet means (37, 126, 181, 243, 290) to admit the gas mixture into the working volume, and outlet means (45, 48; 125, 138; 183, 187; 247, 248; 284, 285) to discharge gas fractions from opposite ends of the regenerator combination,

(d) the reciprocating means subjecting the gas flow to cyclical reversals of pressure and direction of flow so that flow under decreased pressure of a first gas fraction past the regenerator combination towards one space is enriched in the first more readily adsorbed component and is discharged through one outlet means, a flow under increased pressure of a second gas fraction past the regenerator combination towards the remaining space is depleted in the first more readily

adsorbed component, and the second gas fraction is removed through another outlet means,

(e) the reciprocating means (35, 110, 162, 221, 281) cooperating with the first and second volume displacement means so that the displacement means reciprocate at the same frequency, and the volume of gas displaced by the first volume displacement means leads the volume of gas displaced by the second volume displacement means by a phase angle of between zero degrees and 180 degrees.

27. An apparatus as claimed in claim 25 or 26 further characterised by the volume displacement means having first (13, 106, 155, 208, 269) and second (11, 106, 156, 212, 272) volume displacement means which communicate with the first and second spaces respectively.

28. An apparatus as claimed in claim 25, 26 or 27, further characterized by:

(a) control means (57, 140) adapted to cooperate with outlet valve means (43, 46; 123; 129; 139; 184, 188; 250, 251) so that the second gas fraction depleted in the more readily adsorbed component is removed from adjacent the first space at a time when the pressure is approximately at its maximum for the cycle, and the first gas fraction enriched in the more readily adsorbed component is removed from adjacent the second space when the pressure is approximately at a minimum for the cycle.

29. An apparatus as claimed in one of claims 25 to 28 further characterised by:

(a) auxiliary heat exchangers (50, 121, 296) provided in the regenerator combination (27, 34; 119, 120; 282, 283) and adapted to transfer heat between portions of the regenerator combination and gas flow relative to either the inlet means or the outlet means.

30. An apparatus as claimed in one of claims 25 to 29 further characterised by:

(a) the reciprocating means (35) cooperating with the volume displacement means (11, 13) so that heat is pumped from the first space (20) to the second space (15, 19),

(b) thermal insulation means (60) cooperating with the first space to enable reduction of the temperature of the first space to permit gas separation at reduced temperature.

31. An apparatus as claimed in one of claims 25 to 30 further characterised by:

(a) means to maintain the temperature (T_1) of the first space (20, 225, 274) higher than the temperature (T_2) of the second space (15, 19; 215, 227; 275, 277),

(b) work conversion means (11, 212, 272) cooperating with the first and second spaces to convert in part heat at the higher temperature to mechanical work or compression so as to operate also as an engine.

32. The apparatus as claimed in claim 25 further characterised by:

(a) the volume displacement means being a double-acting displacer means (106, 155), so that phase angle between first and second gas volume displacements is 180 degrees,

characterised by:

(a) a catalyst (308) located in the reaction zone (274) to enhance rate of the reaction.

41. An apparatus as claimed in claim 39 further characterised by:

(a) the chemical reaction being exothermic,

(b) the reaction zone being located adjacent the first space (274) of the working volume to supply heat in the first space, so as to convert a portion of reaction heat to mechanical energy.

42. An apparatus as claimed in claim 39 further characterised by:

(a) the chemical reaction being endothermic,

(b) the reaction being located in the second space (275) so that heat required by the reaction is transported from the first space to the second space by heat pump action.

43. An apparatus as claimed in claim 39 further characterised by:

(a) condenser means (302) cooperating with the second space (275) of the apparatus so as to liquefy at least one product of the reaction, so as to facilitate separation of the product.

44. An apparatus as claimed in one of claims 25 to 43, further characterised by:

(a) the volume displacement means including first (13, 106, 155, 208, 269) and second (11, 106, 156, 212, 272) volume displacement means which are adapted to reciprocate at the same frequency, and at respective amplitudes of reciprocation with the displacement phase angle being approximately 90 degrees, the first and second displacement means communicating with the first and second spaces respectively,

(b) the ratio of the amplitudes of the displacements of the first and second displacement means being approximately equal to the ratio of the higher temperature to the lower temperature of the spaces, when expressed in degrees Kelvin.

45. An apparatus as claimed in one of claims 25 to 44, further characterised by:

(a) the regenerator combination having a chamber containing the adsorbent material (34, 120, 189, 239, 283) integral with the thermal regenerator (27, 119, 175, 238, 282).

Patentansprüche

1. Verfahren zum Trennen von Komponenten eines Gasgemischs mit einer ersten Komponente, die von einem adsorbierenden Material leichter adsorbiert wird, und einer zweiten Komponente, die weniger leicht adsorbiert wird,

mit den Verfahrensschritten,

daß das Gasgemisch in eine Arbeitsvolumen mit einer Strömungsbahn eingeführt wird (37, 126, 181, 243, 290), die in einem Adsorberbett das adsorbierenden Material (34, 120, 189, 239, 283) enthält,

daß die Strömungsrichtung des Gasgemischs längs der Strömungsbahn zyklisch umgekehrt wird, so daß die Richtung der Strömung zwischen entgegengesetzten Enden der Strömungsbahn wechselt, wobei der Gesamtdruck des Gasgemischs in dem Arbeitsvolumen zyklisch zwischen

einer oberen und einer unteren Druckgrenze variiert,

daß gleichzeitig die Phasenrelation zwischen den zyklischen Druckänderungen und den zyklischen Strömungsumkehrungen relativ zu dem Adsorberbett so koordiniert wird, daß die erste Komponente durch vergrößerten Druck in den Adsorberbett bevorzugt adsorbiert und festgelegt wird, wenn das Gas in einer Richtung (72) fließt, und die erste Komponente bevorzugt desorbiert wird, wenn der Druck verringert und die Strömung umgekehrt wird (73),

daß in der Nähe eines Endes (42, 133, 180, 252, 276) des Adsorberbetts eine erste Gasfraktion entnommen wird, die mit der ersten Komponente angereichert ist, und in der Nähe des entgegengesetzten Endes (41, 118, 174, 255, 273) des Adsorberbetts eine zweite Gasfraktion, die bezüglich der ersten Komponentens verarmt ist,

daß in der Strömungsbahn erste (20, 11, 163, 225, 274) und zweite (15, 19, 130; 165; 208, 215; 275, 277) Räume vorgesehen werden, die in der Nähe entgegengesetzten Enden der Regeneratorkombination angeordnet sind, wobei dieses Räume sich auf unterschiedlichen Temperaturen befinden, so daß die Regeneratorkombination einem Wärmegradienten ausgesetzt ist, und

daß die Gasströmung durch die Räume und die in Reihe dazu angeordnete Regeneratorkombination geleitet wird,

dadurch gekennzeichnet,

daß in der Strömungsbahn ein Wärmeregenerator (27, 119, 238, 282) vorgesehen wird, der im Zusammenwirken mit dem Adsorberbett eine Adsorber/Regeneratorkombination (34, 27; 120, 119; 189, 175; 239, 238; 283, 282) bildet,

daß die längs der Strömungsbahn verlaufende Strömung durch die Adsorber/Regeneratorkombination geleitet wird,

und daß die zyklischen Druckänderungen und die zyklische Strömungsumkehr durch erste zyklische Gasvolumenverschiebungen in Verbindung mit dem ersten Raum (20, 111, 163, 225, 274) und durch zweite zyklische Gasvolumenverschiebungen in Verbindung mit dem zweiten Raum (15, 19; 113; 165; 208, 215; 275, 277) so erzeugt werden, daß die ersten zyklischen Gasvolumenverschiebungen einen gegenüber den zweiten zyklischen Gasvolumenverschiebungen vauseilenden Phasenwinkel haben, so daß die Gasströmung zusammen mit den zyklischen Umkehrungen des Drucks und der Strömungsrichtung zyklischen Temperaturumsteuerungen unterworfen wird und dadurch die Trennung des Gases in die erste und die zweite Gasfraktion erleichtert und eine Umwandlung zwischen thermischer Energie und Kompressionsenergie in dem Gasgemisch herbeigeführt werden.

2. Verfahren zum Betreiben einer modifizierten Stirling-Maschine, in der ein inneres Arbeitsvolumen, das ein Gas enthält, eine Strömungsbahn aufweist, die einen ersten (20, 111, 163, 225, 274) und einen zweiten Raum (15, 19; 113; 165; 208, 215; 275, 277) und einen zwischen diesen angeordneten Wärmeregenerator (27, 119, 238, 282)

ponente verarmte zweite Gasfraktion aus der Nähe des ersten Endbereichs des Betts weggeschafft wird,

c) und daß ein Teil der dem ersten Raum zugeführten Wärme in mechanische Arbeit oder Kompressionsarbeit umgewandelt wird, so daß man die Arbeitsweise eines Motors erhält.

8. Verfahren nach einen der Ansprüche 1 bis 6, bei dem die Regeneratorkombination (27, 34; 119, 120; 175, 189; 238, 239; 282, 283) einen ersten (41, 118, 174, 255, 273) und einen zweiten (42, 133, 180, 252, 276) Endbereich aufweist, die dem ersten (20, 111, 163, 225, 274) bzw. dem zweiten (15, 19, 113, 165, 208, 215; 275, 277) Raum zugeordnet sind,

dadurch gekennzeichnet,

a) daß der erste Raum auf einer höheren Temperatur gehalten wird als der zweite Raum,

b) daß aus der Nähe des zweiten Endbereichs der Kombination die bezüglich der leichter adsorbierten ersten Komponenten angereicherte erste Gasfraktion entfernt und aus der Nähe des Endbereichs der Kombination die bezüglich der ersten Komponenten verarmte Gasfraktion entfernt wird,

c) daß Wärme von dem ersten Raum zu dem zweiten Raum transportiert wird, so daß man die Arbeitsweise eines Wärmepumpenzyklus oder eines Kühlzyklus erhält.

9. Verfahren nach Anspruch 8, dadurch gekennzeichnet,

a) daß der erste Raum (20), der erste Endbereich (41) der Regeneratorkombination sowie ein Teil (24, 28) der zwischen dem ersten Raum und dem ersten Endbereich verlaufenden Strömungsbahn (mittels 60) isoliert wird, um in dem ersten Endbereich der Regeneratorkombination das Erreichen niedriger Temperaturen zu ermöglichen und die Gastrennung zu begünstigen.

10. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet,

(a) daß die Phasenrelation zwischen den Druck- und Strömungsumkehrungen koordiniert wird, um erste zyklische Gasvolumenverschiebungen in der Nähe eines ersten Endbereichs (118, 174) der Regeneratorkombination (119, 120; 175, 189) zu erzeugen, die einen um 180° vorausseilenden Phasenverschiebungswinkel gegenüber zweiten zyklischen Gasvolumenverschiebungen haben, die in der Nähe des entgegengesetzten zweiten Endbereichs (131, 180) der Regeneratorkombination erzeugt werden, wobei das Arbeitsvolumen im wesentlichen konstant gehalten wird, und

(b) daß ein Teil der dem relativ wärmeren Raum (111, 163) zugeführten Wärme in Kompressionsenergie umgewandelt wird, indem wenigstens eine abgetrennte Gasfraktion zugeführt wird, deren Druck größer ist als der Druck, mit dem das Gasgemisch in den Prozeß eingeführt wird, so daß das Verfahren als ein Thermo-Kompressorzyklus abläuft.

11. Verfahren nach Anspruch 1, dadurch gekennzeichnet,

(a) daß in einem ersten Abschnitt (150) der Strömungsbahn die Phasenrelation zwischen den

Druck- und Strömungsumkehrungen so koordiniert wird, daß in der Nähe eines ersten Endbereichs (174) der Regeneratorkombination Gasvolumenverschiebungen erzeugt werden, die gegenüber zweiten zyklischen Gasvolumenverschiebungen, die in der Nähe des entgegengesetzten Endbereichs der Regeneratorkombination erzeugt werden, einen um 180° vorausseilenden Phasenverschiebungswinkel haben, wobei das Arbeitsvolumen des ersten Abschnitts im wesentlichen konstant gehalten wird,

(b) daß in einem zweiten Abschnitt (151) der Strömungsbahn ein zweiter Wärmegenerator (190) vorgesehen wird und in diesem zweiten Abschnitt der Strömungsbahn die Strömungsrichtung zyklisch umgekehrt wird, so daß die Strömungsrichtung zwischen entgegengesetzten Enden der Strömungsbahn zyklisch wechselt, wobei der zweite Wärmegenerator einem Wärmegradienten ausgesetzt wird, so daß der Gasdruck zwischen einer oberen und einer unteren Druckgrenze zyklisch variiert und in dem zweiten Abschnitt eine zweite Phasenrelation besteht, bei der erste zyklische Gasvolumenverschiebungen, die in der Nähe eines ersten Endbereichs des zweiten Wärmeregenerators (190) erzeugt werden, gegenüber zweiten zyklischen Gasvolumenverschiebungen, die in der Nähe des entgegengesetzten zweiten Endbereichs des zweiten Wärmeregenerators erzeugt werden, einen um 180° vorausseilenden Phasenverschiebungswinkel haben, wobei das zweite Arbeitsvolumen im wesentlichen konstant gehalten wird,

(c) daß der erste und der zweite Abschnitt (150, 151) der Strömungsbahn miteinander verbunden werden, um eine gewünschte Phasenrelation zwischen den Strömungsrichtungsumkehrungen und den Druckänderungen des ersten und des zweiten Abschnitts der Vorrichtung zu erhalten, so daß für den Betrieb als Thermo-Kompressor größere Flexibilität und Druckdifferenzen erreicht werden.

12. Verfahren nach Anspruch 11, dadurch gekennzeichnet,

(a) daß in dem zweiten Abschnitt (151) der Strömungsbahn Umkehrungsbewegungen größerer Gasvolumina vorgesehen sind als in dem ersten Abschnitt (150) der Strömungsbahn, so daß Druckänderungen aus dem zweiten Abschnitt im ersten Abschnitt dominieren.

13. Verfahren nach Anspruch 11 oder 12, dadurch gekennzeichnet,

(a) daß in der Regeneratorkombination (175, 189) des ersten Abschnitts (150) und in dem Wärmegenerator (190) des zweiten Abschnitts (151) im wesentlichen gleiche Wärmegradienten mit im wesentlichen gleichen oberen Temperaturen (T_1 , T_3) und im wesentlichen gleichen unteren Temperaturen (T_2) vorgesehen werden, wobei der erste Raum (163, 168) jedes Abschnitts der oberen Temperaturen ausgesetzt wird, so daß man einen Betrieb als Thermo-Kompressor mit verbesserter Phasenrelation erhält.

14. Verfahren nach Anspruch 11 oder 12, dadurch gekennzeichnet,

23. Verfahren nach Anspruch 18 oder 19, dadurch gekennzeichnet, daß wenigstens ein Produkt der Reaktion in einem Kühlraum (277) der Vorrichtung verflüssigt wird, um die Trennung des Produkts zu erleichtern.

24. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet,

(a) daß zwischen Abschnitten der Regeneratorkombination (27, 34; 119, 120; 282, 283) und der Gasströmung Wärme entweder zu der Einlaßeinrichtung (37, 126, 290) oder der Auslaßeinrichtung (48, 125) übertragen wird.

25. Vorrichtung zum Trennen von Komponenten eines Gasgemischs mit einer ersten Komponente, die von einem adsorbierenden Material (10, 102, 148, 201, 266) leichter adsorbiert wird, und einer zweiten Komponente, die weniger leicht adsorbiert wird,

mit einem Körper mit einem inneren Arbeitsvolumen mit einem ersten (20, 111, 163, 225, 274) und einem zweiten (15, 19; 113; 165; 215, 227; 275, 277) Raum, einer den ersten und den zweiten Raum verbindenden Strömungsbahn und einem das adsorbierende Material enthaltenden Adsorberbett, das zwischen den Räumen in den Strömungsweg angeordnet ist,

mit einer Einlaßeinrichtung (37, 126, 181, 243, 290) zum Einführen des Gasgemischs in das Arbeitsvolumen und einer Auslaßeinrichtung (45, 48; 125, 138; 183, 187; 247, 248; 284, 284) zum Entnehmen von Gas in der Nähe der entgegengesetzten Endbereiche (41, 42; 118, 133; 174, 180; 255, 256; 273, 276) des Adsorberbetts,

mit dem ersten und dem zweiten Raum zugeordneten Mitteln (13, 11; 106; 155, 156; 208, 212; 269, 272) zur Volumenverschiebung,

mit Mitteln (35, 110, 162, 221, 281) zur Erzeugung einer Hin- und Herbewegung, die mit der Einrichtung zur Volumenverschiebung derart zusammenwirken, daß zyklische Änderungen des Gesamtdrucks und zyklische Umkehrungen der Strömungsrichtung des Gases erzeugt werden, wobei diese Mittel zum Hin- und Herbewegen eine solche Phasenbeziehung zwischen den zyklischen Änderungen des Gasdrucks und der Richtung der Strömung des Gases über dem Adsorberbett herstellen, daß unter reduziertem Druck über das Adsorberbett in Richtung auf einem der Räume verlaufende Strömung bezüglich der leichter adsorbierten ersten Komponente angereichert wird, während die unter erhöhtem Druck über das Adsorberbett in Richtung auf den entgegengesetzten Raum entgegengesetzte Strömung bezüglich der leichter adsorbierten ersten Komponenten verarmt wird,

wobei die Vorrichtung gekennzeichnet ist durch

(a) einen Wärmeregenerator (27, 119, 175, 238, 282), der mit dem Adsorberbett zusammenwirkt und mit diesem eine Adsorber/Regeneratorkombination (27, 34; 119, 120; 175, 189; 238, 239; 282, 283) bildet, die in der Strömungsbahn zwischen den genannten Räumen liegt, und eine längs der Strömungsbahn fließende Strömung aufnimmt, und

(b) Mittel, die den ersten und den zweiten Raum

auf unterschiedlichen Temperaturen (T_1 , T_2) halten und so die Regeneratorkombination einem Wärmegradienten aussetzen, so daß die Gasströmung zusätzlich mit den zyklischen Druck- und Richtungsänderungen zyklischen Temperaturänderungen unterworfen ist, wodurch die Trennung des Gasgemischs in eine bezüglich der ersten Komponente angereicherte erste Gasfraktion und eine bezüglich der zweiten Komponente angereicherte zweite Gasfraktion erleichtert wird, wobei

(c) die Mittel (35, 110, 162, 221, 281) zur Erzeugung der Hin- und Herbewegung mit den ersten und zweiten Mitteln zur Volumenverschiebung so zusammenwirken, daß letztere sich mit gleicher Frequenz hin- und herbewegen und das von den ersten Mitteln zur Volumenverschiebung bewegte Gasvolumen dem von den zweiten Mitteln zur Volumenverschiebung bewegten Gasvolumen mit einem zwischen Null und 180° liegendem Phasenwinkel vorausschleift.

26. Vorrichtung (10, 102, 148, 201, 266) nach Art einer modifizierten Stirling-Kraftmaschine

mit einem Körper mit einem internen Arbeitsvolumen mit einem ersten (20, 111, 163, 225, 274) und einem zweiten (15, 19; 113; 165; 215, 227; 275, 277) Raum, einer Strömungsbahn zur gasführenden Verbindung des ersten mit dem zweiten Raum und einem in der Strömungsbahn zwischen dem ersten und dem zweiten Raum angeordneten Wärmeregenerator (27, 119, 175, 238, 282), wobei der erste und der zweite Raum auf unterschiedlichen Temperaturen (T_1 , T_2) liegen, so daß der Regenerator einem Wärmegradienten ausgesetzt ist,

mit ersten (13, 106, 155, 208, 269) und zweiten (11, 106, 156, 212, 272) Mitteln zur Volumenverschiebung, die mit dem ersten bzw. dem zweiten Raum in Verbindung stehen,

mit Mitteln (35, 110, 162, 221, 281) zur Erzeugung einer Hin- und Herbewegung, die mit den ersten und zweiten Mitteln zur Volumenverschiebung derart zusammenwirken, daß letztere sich mit gleicher Frequenz hin- und herbewegen, um zyklische Änderungen des Gesamtdrucks und der Strömungsrichtung des Gases zu erzeugen, wobei die Mittel zum Hin- und Herbewegen den Phasenwinkel zwischen den zyklischen Druckänderungen in dem Gas und der zyklischen Richtungsänderungen des Gases über dem Wärmeregenerator bestimmen,

dadurch gekennzeichnet,

(a) daß ein Adsorberbett vorgesehen ist, das adsorbierendes Material (34, 120, 189, 239, 283) enthält und im Zusammenwirken mit dem Wärmeregenerator eine zwischen dem ersten und dem zweiten Raum angeordnete Adsorber/Regeneratorkombination (27, 34; 19, 120; 175, 189; 238, 239; 282, 283) bildet,

(b) daß das Gas ein Gasgemisch ist mit einer ersten Komponente, die von einem adsorbierenden Material leichter adsorbiert wird, und einer zweiten Komponente, die weniger leicht adsorbiert wird,

(c) daß eine Einlaßeinrichtung (37, 126, 181,

gung unter einem Phasenwinkel zusammenwirken, der zyklische Druckänderungen und Richtungsumkehrungen der Gasströmung über die Regeneratorkombination koordiniert, um die Trennung der Komponenten zu verbessern.

34. Vorrichtung nach Anspruch 32, dadurch gekennzeichnet,

(a) daß der Wärmegradient der Regeneratorkombination (175, 189) durch die dem ersten (163) bzw. dem zweiten (165) Raum zugeordnete erste (T_1) bzw. zweite (T_2) Temperatur bestimmt wird, wobei die zweite Temperatur in der Nähe der Umgebungstemperatur liegt,

(b) daß ein zweiter Abschnitt (151) der Strömungsbahn eine zweite doppelwirkende Verdrängereinrichtung (156) und einen zweiten Verdrängungszylinder (154) enthält, wobei die zweite doppelwirkende Verdrängereinrichtung innerhalb des zweiten Verdrängerzylinders hin- und herbewegbar ist,

(c) daß ein zweiter Wärmeregenerator (190) vorgesehen ist, der mit entgegengesetzten Endbereichen des zweiten Verdrängungszylinders zusammenwirkt und einem zweiten Wärmegradienten ausgesetzt ist, der durch die zweite Temperatur (T_2) und eine dritte Temperatur (T_3) bestimmt ist, wobei die dritte Temperatur größer ist als die Umgebungstemperatur, und

(d) daß Mittel (195) vorgesehen sind, die Vorrichtung Wärme mit der dritten Temperatur zuführen, so daß die Verdrängereinrichtung und die Mittel zur Hin- und Herbewegung so betrieben werden, daß sowohl eine Gastrennung als auch eine Kühlmaschinenfunktion erreicht werden.

35. Vorrichtung nach Anspruch 33 oder 34, dadurch gekennzeichnet,

(a) daß die zweite doppelwirkende Verdrängereinrichtung (165) eine größere Verdrängung hat als die erste doppelwirkende Verdrängereinrichtung (155), so daß sie für die Änderungen der Gasströmung und des Gasdrucks in dem Arbeitsvolumen dominierend ist.

36. Vorrichtung nach einem der Ansprüche 25 bis 35, dadurch gekennzeichnet,

(a) daß die Adsorber/Regeneratorkombination (238, 239) einen mittleren Abschnitt (253) aufweist, der zwischen den entgegengesetzten ersten (249) und zweiten (256) Endbereichen der Regeneratorkombination so angeordnet ist, daß der erste (255) und der zweite (256) Abschnitt der Regeneratorkombination zwischen dem mittleren Abschnitt und dem ersten bzw. dem zweiten Endbereich der Regeneratorkombination liegen, und

(b) daß das Arbeitsvolumen einen dritten Raum (229) umfaßt, der über eine Zwischenleitung (231) mit dem mittleren Abschnitt verbunden ist, wobei die Mittel (208) zur Volumenverschiebung im Zusammenwirken mit dem dritten Raum zyklische Strömungsrichtungsumkehrungen des Gases zwischen dem dritten Raum und dem mittleren Abschnitt erzeugen.

37. Vorrichtung nach Anspruch 36, dadurch gekennzeichnet,

(a) daß die Mittel (221) zur Erzeugung der Hin-

und Herbewegung mit den Mitteln (208) zur Volumenverschiebung so zusammenwirken, daß die zyklischen Strömungsumkehrungen zwischen dem dritten Raum (229) und dem mittleren Abschnitt (253) der Regeneratorkombination gleichphasig gehalten werden mit den zyklischen Strömungsumkehrungen zwischen dem ersten Raum (225) und dem ersten Abschnitt (255) der Kombination, und

(b) daß die Mittel (208) zur Volumenverschiebung derart mit dem ersten (227), dem zweiten (215) und dem dritten (229) Raum zusammenwirken, daß die Gasströmung durch den zweiten Abschnitt (256) der Kombination größer ist als durch den ersten Abschnitt der Kombination.

38. Vorrichtung nach Anspruch 37, dadurch gekennzeichnet,

(a) daß die Mittel (221) zur Hin- und Herbewegung mit den Mitteln (208) zur Volumenverschiebung derart zusammenwirken, daß zyklische Gasvolumenverschiebungen in der Nähe des ersten Endbereichs (249) der Regeneratorkombination (238, 239) einen den zyklischen Gasvolumenverschiebungen in der Nähe des zweiten Endbereichs (252) der Regeneratorkombination voraus-eilenden Phasenverschiebungswinkel haben, und

(b) daß im Bereich des mittleren Abschnitts (253) und der Zwischenleitung (231) Isoliermittel (255) vorgesehen sind, so daß die Temperatur im Bereich des mittleren Abschnitts und der Zwischenleitung im Vergleich zu der Temperatur an den beiden Enden der Regeneratorkombination abgesenkt ist.

39. Vorrichtung nach einem der Ansprüche 25 bis 38, gekennzeichnet durch

(a) Mittel zur Herbeiführung einer chemischen Reaktion in einer Reaktionszone in dem Arbeitsvolumen, in der das Gasgemisch wenigstens einen Reaktionspartner und wenigstens ein Produkt der chemischen Reaktion enthält, wobei

(b) die Regeneratorkombination (282, 283) so ausgebildet ist, daß sie wenigstens eines der Produkte adsorbiert und so wenigstens ein Teil des Produkts von dem Gasgemisch getrennt wird, um die Reaktion aus dem Gleichgewicht zu führen und hohen Umwandlungsgrad zu erzielen.

40. Vorrichtung nach Anspruch 39, dadurch gekennzeichnet,

(a) daß zur Erhöhung der Reaktionsgeschwindigkeit in der Reaktionszone (274) ein Katalysator (308) vorgesehen sind.

41. Vorrichtung nach Anspruch 39, dadurch gekennzeichnet,

(a) daß die chemische Reaktion eine exotherme Reaktion ist und Reaktionswärme erzeugt und

(b) daß die Reaktionszone in der Nähe des ersten Raums (274) des Arbeitsvolumens liegt, um dem ersten Raum Wärme zuzuführen und so einen Teils der Reaktionswärme in mechanische Energie umzuwandeln.

42. Vorrichtung nach Anspruch 39, dadurch gekennzeichnet,

(a) daß die chemische Reaktion eine endotherme Reaktion ist und

(b) daß die Reaktionszone in dem zweiten Raum

pression et les inversions cycliques de circulation relatives aux régénérateurs thermiques, le procédé étant caractérisé par

(a) la disposition, entre lesdits espaces, d'un lit adsorbant contenant une matière adsorbante (34, 120, 189, 239, 283) et destiné à coopérer avec le régénérateur thermique afin qu'ils constituent une combinaison formant adsorbant-régénérateur,

(b) l'introduction (37, 126, 181, 243, 290) dans le volume de travail, d'un mélange de gaz contenant un premier constituant qui est adsorbé plus facilement par la matière adsorbante et un second constituant qui est adsorbé moins facilement par la matière adsorbante,

(c) la création des variations cycliques de pression et des inversions cycliques de circulation par des premiers déplacements cycliques d'un volume de gaz associés au premier espace (20, 111, 163, 225, 274) et par des seconds déplacements cycliques d'un volume de gaz associés au second espace (15, 19; 113; 165; 208, 215; 275, 277) afin que les premiers déplacements cycliques d'un volume de gaz présentent un angle de phase en avance par rapport aux seconds déplacements cycliques d'un volume de gaz,

(d) simultanément, lors de la coordination de la relation de phase entre les variations cycliques de pression et les inversions cycliques de sens de circulation relatives à la combinaison formant régénérateur, l'adsorption et l'immobilisation préférentielles du premier constituant sur le lit combiné par augmentation de la pression lorsque le gaz circule dans un premier sens (72) et la désorption préférentielle du premier constituant par réduction de la pression lorsque le sens de circulation est inversé (73), et

(e) l'extraction, à partir d'une première extrémité (42, 133, 180, 252, 276) de la combinaison formant régénérateur, d'une première fraction gazeuse enrichie en premier constituant, et l'extraction, de l'extrémité opposée (41, 118, 174, 255, 273) de la combinaison formant régénérateur, d'une seconde fraction gazeuse appauvrie en premier constituant, si bien qu'une conversion entre l'énergie thermique et l'énergie de compression est aussi obtenue dans le mélange de gaz.

3. Procédé selon la revendication 1 ou 2, caractérisé en outre par

(a) le transport de chaleur du premier espace au second espace, le premier espace étant à une première température (T_1) et le second espace étant à une seconde température (T_2), et

(b) l'extraction de la première fraction gazeuse enrichie en premier constituant de la proximité d'une seconde extrémité (42, 133, 180, 252, 276) de la combinaison formant régénérateur qui est adjacente au second espace, et l'extraction de la seconde fraction gazeuse appauvrie en premier constituant de la proximité d'une première extrémité (41, 118, 174, 255, 273) de la combinaison formant régénérateur, qui est adjacente au premier espace.

4. Procédé selon la revendication 1, 2 ou 3, caractérisé en outre par

(a) l'extraction de la seconde fraction gazeuse

appauvrie en constituant adsorbé préférentiellement du volume de travail au moment où la pression est approximativement maximale dans le cycle, et

(b) l'extraction de la première fraction gazeuse enrichie en constituant adsorbé le plus facilement lorsque la pression est approximativement minimale au cours du cycle.

5. Procédé selon l'une quelconque des revendications précédentes, caractérisé en outre en ce que

(a) pour la création des inversions cycliques de sens de circulation et des variations de pression dans le volume de travail, un premier dispositif (13, 106, 155, 208, 269) et un second dispositif (11, 106, 156, 212, 272) de déplacement volumique sont déplacés en translation afin qu'ils communiquent avec le premier espace (20, 111, 163, 225, 274) et le second espace (15, 19; 113; 165; 208, 215; 275, 277) respectivement pour une première et une seconde amplitude de déplacement alternatif respectivement, le rapport des amplitudes des déplacements étant approximativement égal au rapport de la température la plus élevée (T_1) à la température la plus faible (T_2) exprimées en kelvins, et le premier dispositif de déplacement volumique à un angle de phase en avance d'environ 90° par rapport au second dispositif de déplacement volumique.

6. Procédé selon l'une quelconque des revendications précédentes, caractérisé en outre par

(a) la disposition du lit adsorbant (34, 120, 189, 239, 283) physiquement dans une chambre contenant le régénérateur thermique (27, 119, 175, 283, 282) afin que la combinaison formant régénérateur forme un ensemble solidaire.

7. Procédé selon l'une quelconque des revendications précédentes, dans lequel la combinaison formant régénérateur (27, 34; 119, 120; 175, 189; 238, 239; 282, 283) a une première extrémité (41, 118, 174, 255, 273) et une seconde extrémité (42, 133, 180, 252, 276) associées au premier espace (20, 111, 163, 225, 274) et au second espace (15, 19, 113; 165; 208, 215; 275, 277) respectivement, et qui se caractérise en outre en ce qu'il comprend:

(a) le maintien du premier espace à une température supérieure à celle du second espace,

(b) l'extraction de la première fraction gazeuse enrichie en premier constituant le plus facilement adsorbé depuis la proximité de la seconde extrémité du lit, et l'extraction de la seconde fraction gazeuse appauvrie en premier constituant de la proximité de la première extrémité du lit, et

(c) la transformation d'une certaine quantité de la chaleur fournie au premier espace en travail mécanique ou en travail de compression afin qu'un fonctionnement d'un cycle moteur soit obtenu.

8. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel la combinaison formant régénérateur (27, 34; 119, 120; 175, 189; 238, 239; 282, 283) a une première extrémité (41, 118, 174, 255, 273) et une seconde extrémité (42, 133, 180, 252, 276) qui sont associées respectivement au premier espace et au second espace, et qui est en

15. Procédé selon la revendication 1 ou 2, caractérisé en outre en ce qu'il comprend

(a) la mise en communication avec la combinaison formant régénérateur (238, 239) dans une partie intermédiaire de combinaison (253) comprise entre la première et la seconde extrémité opposée (249, 252) de la combinaison formant régénérateur, afin que la première et la seconde partie (255, 256) de combinaison soient placées entre la partie intermédiaire (253) et la première et la seconde extrémité respectivement de la combinaison formant régénérateur, et

(b) l'inversion cyclique du sens de circulation au niveau de la partie intermédiaire de combinaison afin que le courant circulant dans la première et la seconde partie de combinaison varie cycliquement.

16. Procédé selon la revendication 15, caractérisé en outre en ce qu'il comprend

(a) le maintien des inversions cycliques de circulation dans la partie intermédiaire (253) de combinaison en phase avec les inversions cycliques de circulation par rapport à la première extrémité (249) de la combinaison formant régénérateur (238, 239), et

(b) l'inversion cyclique des sens de circulation, dans la partie intermédiaire (253), afin qu'une plus grande quantité de gaz circule dans la seconde partie de combinaison (256) que dans la première (255), si bien que l'écoulement de la chaleur dans la partie intermédiaire et dans la première et la seconde partie de combinaison permet un gain résultant ou une perte résultante de chaleur dans la partie intermédiaire.

17. Procédé selon la revendication 16, caractérisé en ce qu'il comporte en outre

(a) la coordination de la relation de phase entre les inversions cycliques de circulation afin que des déplacements cycliques d'un volume de gaz à proximité de la première extrémité (249) de la combinaison formant régénérateur (238, 239) présentent un angle de phase de déplacement en avance par rapport aux déplacements cycliques d'un volume de gaz près de la seconde extrémité de la combinaison formant régénérateur, et

(b) la disposition d'une isolation (259) près de la partie intermédiaire (253) et des conduits associés (231) afin que la température à proximité de la partie intermédiaire et aux conduits associés soit inférieure aux températures aux deux extrémités (293, 252) de la combinaison formant régénérateur.

18. Procédé selon la revendication 1 ou 2, caractérisé en outre en ce qu'il comprend

(a) l'exécution d'une réaction chimique dans une zone réactionnelle, le mélange de gaz comprenant au moins un réactif et au moins un produit de la réaction, l'un d'eux étant adsorbé préférentiellement sur la matière adsorbante,

(b) la séparation du réactif et du produit par pompage paramétrique sur la matière adsorbante afin que la réaction soit déplacée vers une conversion élevée, et

(c) le transport de chaleur, par rapport à la zone réactionnelle, afin que la température de cette

zone réactionnelle soit maîtrisée.

19. Procédé selon la revendication 1 ou 2, caractérisé en outre en ce qu'il comprend

(a) l'exécution d'une réaction chimique dans une zone réactionnelle, le mélange de gaz comprenant au moins un réactif de la réaction, au moins un produit voulu d'une réaction chimique voulue, et au moins un produit indésirable d'une réaction secondaire, l'un des produits étant adsorbé préférentiellement sur la matière adsorbante,

(b) le transport, par pompage paramétrique, du produit voulu à distance de la zone réactionnelle afin que le maintien hors d'équilibre voulu de la réaction soit facilité et facilite l'obtention d'un rendement élevé de conversion en produit voulu, et

(c) le piégeage, par pompage paramétrique, du produit indésirable présent dans la zone réactionnelle afin que le retardement de la réaction indésirable à proximité de l'équilibre soit facilité et que la transformation en produit indésirable soit réduite.

20. Procédé selon la revendication 18 ou 19, caractérisé en outre en ce qu'il comprend

(a) la disposition d'un catalyseur (308) dans la zone réactionnelle (274) afin que la vitesse de la réaction soit accrue.

21. Procédé selon la revendication 18 ou 19, caractérisé en outre en ce que

(a) la réaction chimique est exothermique et dégage de la chaleur de réaction,

(b) la zone réactionnelle est placée près du premier espace (274) afin que la chaleur de réaction s'ajoute à la chaleur présente dans le premier espace et facilite le fonctionnement en moteur thermique.

22. Procédé selon la revendication 18 ou 19, caractérisé en outre en ce que

(a) la réaction chimique est endothermique et adsorbe de la chaleur de réaction, et

(b) la zone réactionnelle est placée près du second espace (275) afin que la chaleur nécessaire à la réaction soit transportée à partir du premier espace.

23. Procédé selon la revendication 18 ou 19, caractérisé en outre en ce qu'il comprend

(a) la liquéfaction d'au moins un produit de la réaction dans un espace refroidisseur (277) de l'appareil afin que la séparation du produit soit facilitée.

24. Procédé selon la revendication 1 ou 2, caractérisé en outre par

(a) le transfert de chaleur entre des parties de la combinaison formant régénérateur (27, 34; 119, 120; 282, 283) et le courant de gaz vers le dispositif d'entrée (37, 126, 290) ou le dispositif de sortie (48, 125).

25. Appareil (10, 102, 148, 201, 266) de séparation de constituants d'un mélange contenant un premier constituant qui est adsorbé plus facilement et un second constituant qui est moins facilement adsorbé par une matière adsorbante (34, 120, 189, 239, 283), l'appareil comprenant un corps ayant un volume interne de travail qui

volumique d'un angle de phase comprise entre 0 et 180°.

27. Appareil selon la revendication 25 ou 26, caractérisé en outre en ce que les dispositifs de déplacement volumique comprenant le premier dispositif (13, 106, 155, 208, 269) et le second dispositif (11, 106, 156, 212, 272) de déplacement en volume communiquent avec le premier et le second espaces respectivement.

28. Appareil selon la revendication 25, 26 ou 27, caractérisé en outre par

(a) un dispositif de commande (57, 140) destiné à coopérer avec une soupape de sortie (43, 46; 123; 129; 139; 184, 188; 250, 251) afin que la seconde fraction gazeuse appauvrie en constituant le plus facilement adsorbé soit extraite de la proximité du premier espace à un moment où la pression est approximativement maximale dans le cycle, et que la première fraction gazeuse enrichie en constituant le plus facilement adsorbé soit extraite de la proximité du second espace lorsque la pression est approximativement minimale pendant le cycle.

29. Appareil selon l'une des revendications 25 à 28, caractérisé en outre par

(a) des échangeurs de chaleur auxiliaires (50, 121, 296) placés dans la combinaison formant régénérateur (27, 34; 119, 120; 282, 283) et destinés à transférer de la chaleur entre des parties de la combinaison formant régénérateur et du courant de gaz, vers le dispositif d'entrée ou le dispositif de sortie.

30. Appareil selon l'une quelconque des revendications 25 à 29, caractérisé en outre en ce que

(a) les dispositifs de déplacement en translation (35) coopèrent avec les dispositifs de déplacement volumique (11, 13) afin que de la chaleur soit pompée du premier espace (20) au second espace (15, 19), et

(b) un dispositif d'isolation thermique (60) coopère avec le premier espace afin qu'il permette une réduction de la température du premier espace et permette ainsi la séparation du gaz à une température réduite.

31. Appareil selon l'une quelconque des revendications 25 à 30, caractérisé en outre par

(a) un dispositif destiné à maintenir la température (T_1) du premier espace (20, 225, 274) à une valeur supérieure à la température (T_2) du second espace (15, 19; 215, 227; 275, 277), et

(b) un dispositif de conversion de travail (11, 212, 272) destiné à coopérer avec le premier et le second espaces afin qu'il transforme partiellement la chaleur à la température relativement élevée en travail mécanique ou en compression de manière que l'appareil fonctionne aussi en moteur.

32. Appareil selon la revendication 25, caractérisé en outre en ce que

(a) les dispositifs de déplacement volumique sont des dispositifs à double effet (106, 155), si bien que l'angle de phase des premier et des second déplacements volumiques est de 180°,

(b) un cylindre de déplacement (104, 153) coopère avec les extrémités opposées (118, 133; 174,

180) de la combinaison formant régénérateur et avec le dispositif de déplacement à double effet, si bien que le dispositif de déplacement à double effet sépare le premier espace (111, 163) du second espace (113, 165), et

(c) la température (T_1) du premier espace (111, 163) est supérieure à la température (T_2) du second espace (113, 165) afin que l'appareil fonctionne en compresseur thermique.

33. Appareil selon la revendication 32, caractérisé en ce que

(a) le gradient thermique de la combinaison formant régénérateur (175, 189) est déterminé par une première température (T_1) et une seconde température (T_2) associées au premier espace (163) et au second espace (165) respectivement, la combinaison formant régénérateur et le cylindre de déplacement constituant une première partie (150) du trajet de circulation,

(b) une seconde partie (151) du trajet de circulation a un second dispositif de déplacement à double effet (156) et un second cylindre de déplacement (154), le second dispositif de déplacement à double effet étant mobile en translation dans le second cylindre de déplacement,

(c) un second régénérateur thermique (190) coopère avec les extrémités opposées du second cylindre de déplacement et est exposé à un second gradient thermique délimité par la seconde température (T_2) et une troisième température (T_3), la troisième température étant pratiquement égale à la première température, et

(d) un dispositif à conduits (172) reliant la première et la seconde parties (150, 151) du trajet de circulation, et le premier et le second dispositifs de déplacement à double effet coopèrent avec les dispositifs de déplacement en translation afin qu'ils travaillent avec un angle de phase qui coordonne les variations cycliques de pression et les inversions de sens du courant de gaz le long de la combinaison formant régénérateur afin que la séparation des constituants soit facilitée.

34. Appareil selon la revendication 32, caractérisé en outre en ce que

(a) le gradient thermique de la combinaison formant régénérateur est déterminé par une première température (T_1) et une seconde température (T_2) associées au premier espace (163) et au second espace (165) respectivement, la seconde température étant proche de la température ambiante,

(b) une seconde partie (151) du trajet de circulation a un second dispositif de déplacement à double effet (156) et un second cylindre de déplacement (154), le second dispositif de déplacement à double effet pouvant se déplacer en translation dans le second cylindre de déplacement,

(c) un second régénérateur thermique (190) communique avec les extrémités opposées du second cylindre de déplacement et est exposé à un second gradient thermique délimité par la seconde température (T_2) et une troisième température (T_3) qui est supérieure à la température ambiante, et

(d) un dispositif destiné à transmettre de la

(a) la combinaison formant régénérateur a une chambre contenant la matière adsorbante (34,

120, 189, 239, 283) qui est solidaire du régénérateur thermique (27, 119, 175, 238, 282).

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FIG. 1

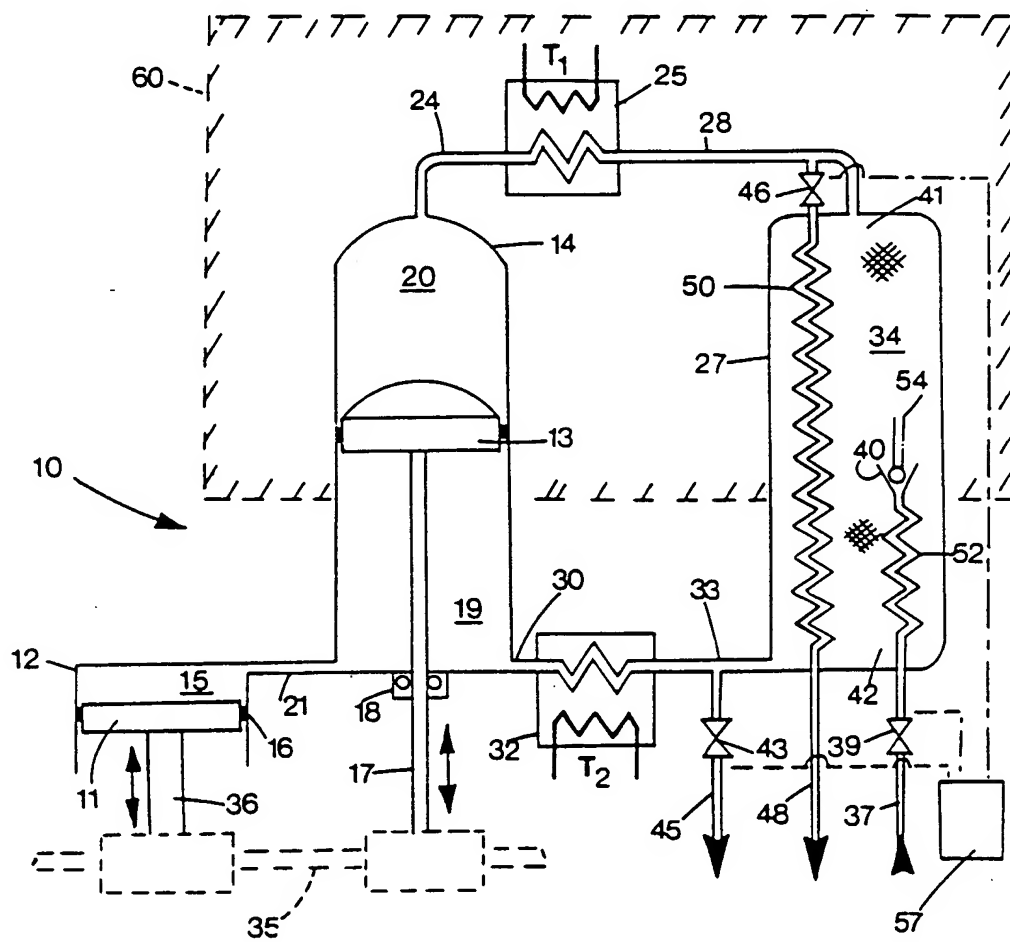


FIG. 2

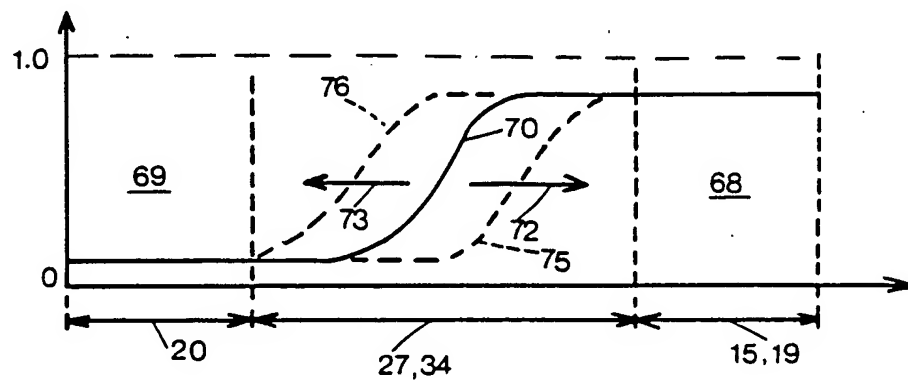


FIG. 3

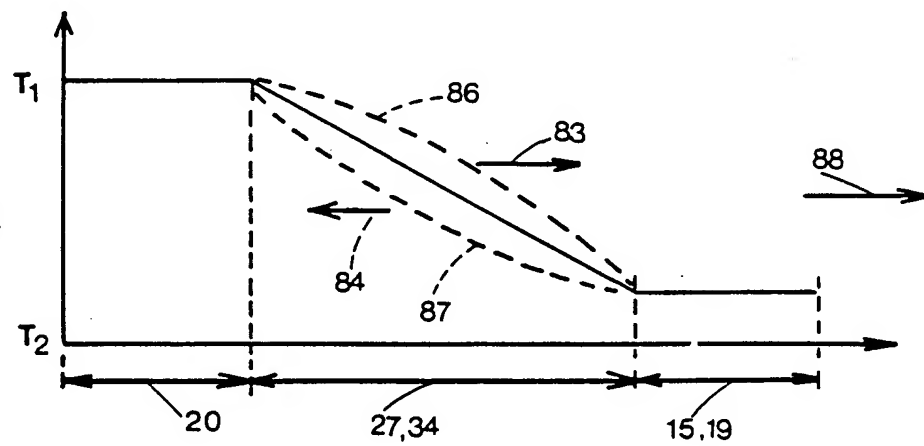


FIG. 4

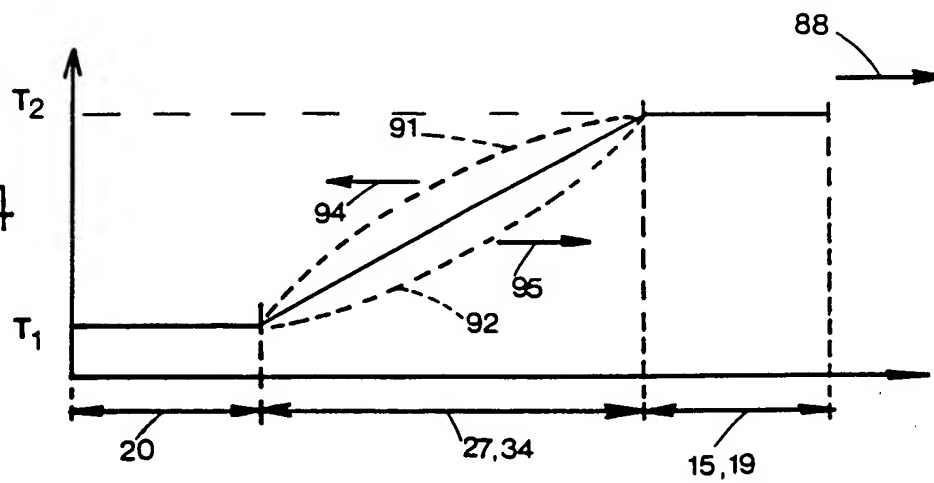
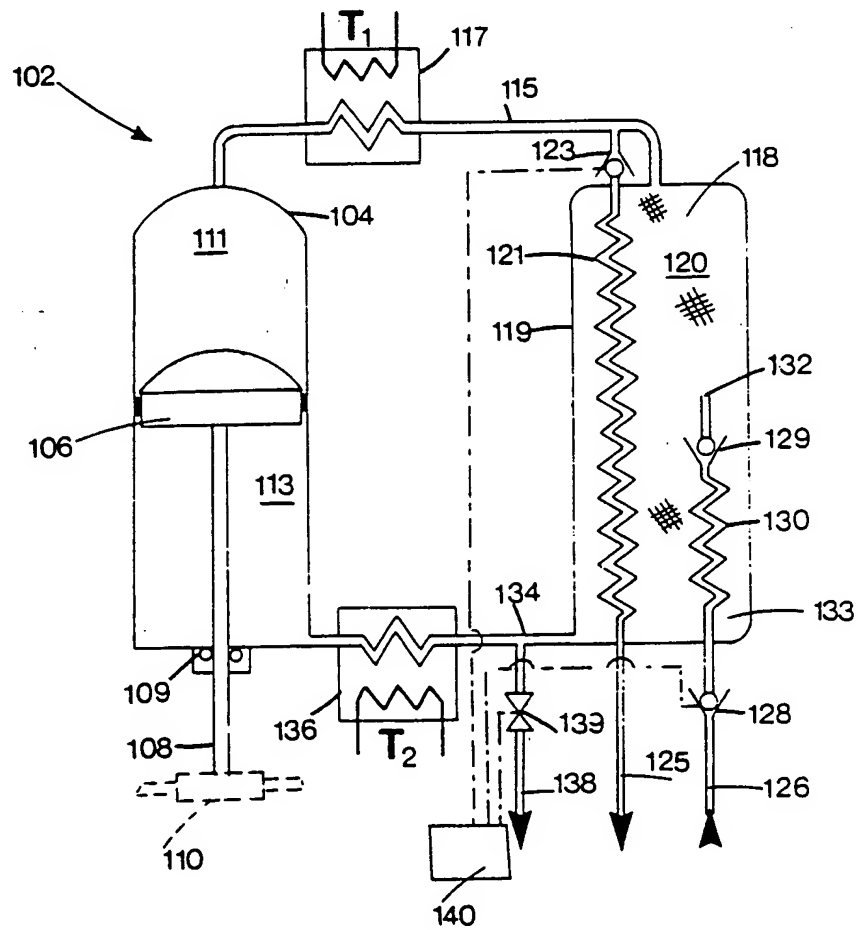


FIG. 5



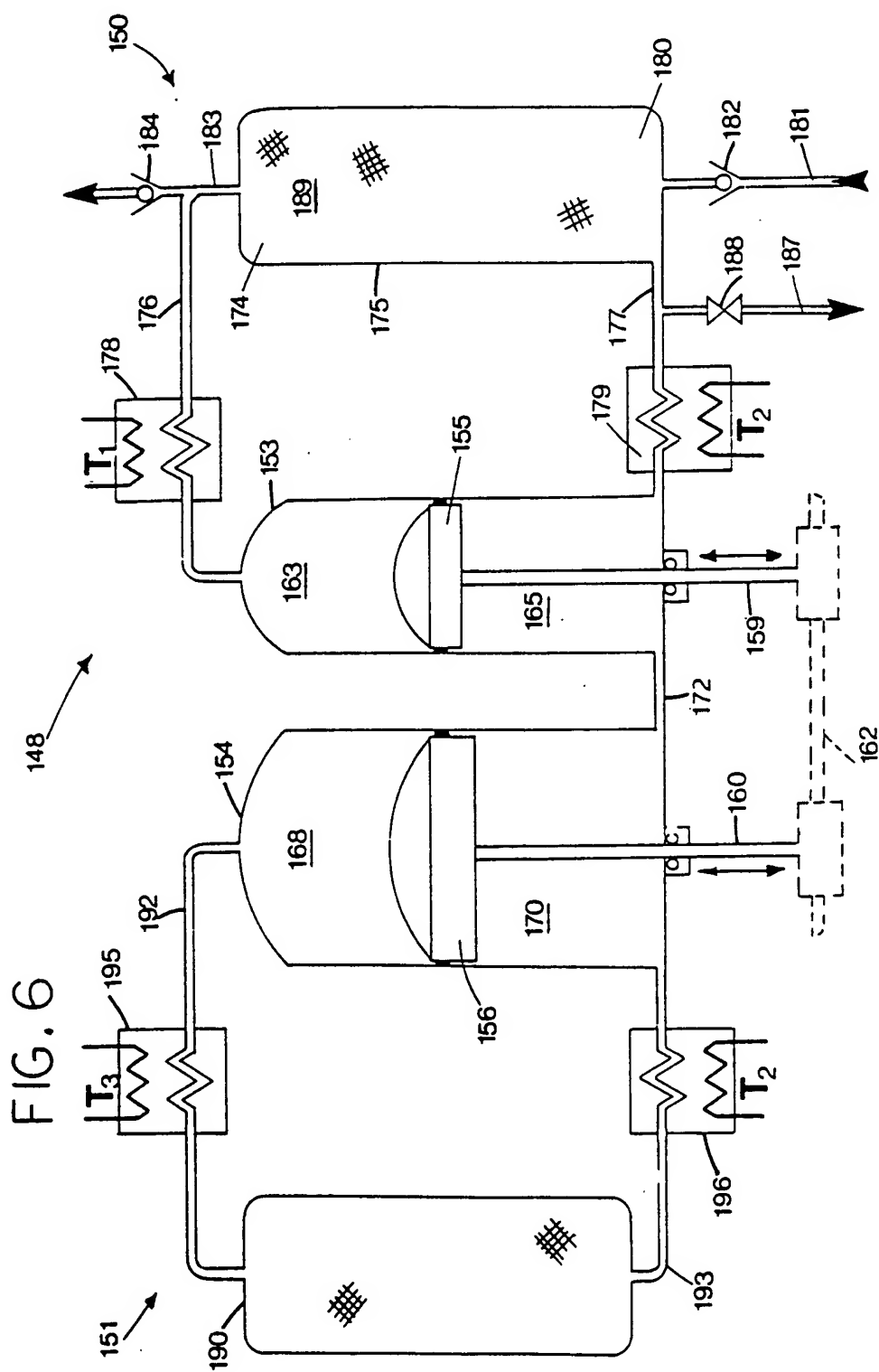


FIG. 7

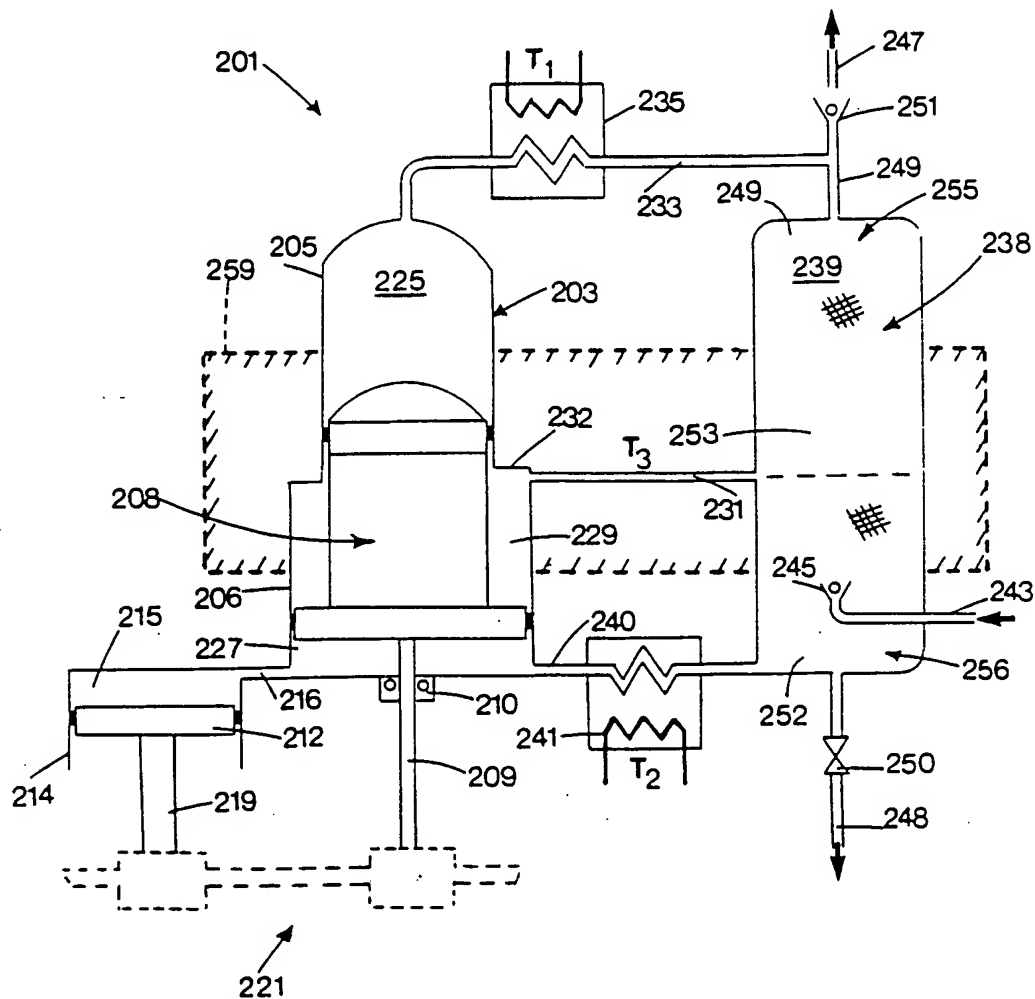


FIG. 8

